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Sulfur dioxide and other sulfur-containing gases have been studied to evaluate their interactions with solids likely to be found in urban aerosols and on ground-level surfaces in the urban environment. Results indicate that sulfur dioxide readily reacts with most of these materials by capacity-limited reactions, particularly at high relative humidities. Removal of hydrogen sulfide and dimethylsulfide over ground-level surfaces is a slow process and largely reversible. The implications of these results with regard to air pollution chemistry and sulfur control strategies are discussed. Publications, reports, and presentations that resulted from this work are listed.

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THE ROLE OF SOLID-GAS INTERACTIONS IN AIR POLLUTION

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ABSTRACT

Sulfur dioxide and other sulfur-containing gases have been studied to evaluate their interaction with solids likely to be found in urban aerosol and on ground-level surfaces in the urban environment. The results of this study indicate that sulfur dioxide readily reacts with most of these materials by capacity-limited reactions, particularly at high relative humidities. Removal of hydrogen sulfide and dimethylsulfide over ground-level surfaces is a slow process and largely reversible. The implications of these results with regard to air pollution chemistry and sulfur control strategies are discussed. Publications, reports, and presentations that resulted from this work are listed.

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SECTION 1

INTRODUCTION

The atmospheric chemistry of sulfur-containing compounds is of considerable interest because of potential adverse health effects attributable to these species as well as acidic rainfalls and haze formation (1). A process of importance in all of these phenomena is the atmospheric transformation of gaseous sulfur dioxide (SO_2) to sulfate aerosol. Several mechanisms, all of which may be operable, have been suggested to account for this transformation (1, 2). These include gas-phase oxidation of SO_2 by direct and indirect photolysis, oxidation in liquid droplets, and oxidation on the surface of atmospheric aerosols.

The latter type of process, involving gas-solid interactions in the atmosphere, is poorly understood and generally neglected by air pollution modelers. Such processes are also important in the removal of pollutant gases from the atmosphere by interaction with ground-level surfaces (1). For these reasons, laboratory studies of SO_2 interactions with solids likely to be found in urban aerosols, and at ground levels in the urban environment, were carried out.

Also of interest were gas-solid interactions, primarily with ground-level surfaces, of biogenically emitted sulfur-containing gases. Emissions of the latter species, on a global scale, are estimated to be comparable to anthropogenic SO_2 emissions (3-5) and consequently are important constituents in atmospheric sulfur budgets. The biogenic sulfur emissions are believed to arise from hydrogen sulfide (H_2S) and dimethylsulfide (3-5), although the relative contributions of these two species are uncertain (4-7). In this work, studies of interactions of both species with selected ground-level surfaces were carried out.

The results of our studies indicate that SO_2 interactions with representative aerosol materials can initially occur quite rapidly. In most cases, this takes place with a near quantitative conversion to adsorbed sulfate. With time (SO_2 exposure), the reactivities of the solids investigated gradually diminish and ultimately approach zero because of the capacity-limited nature of these reactions. Atmospheric projections of our results with the use of simple models for gas-solid interactions indicate that these processes will be most important at or near emission sources, e.g., in power plant plumes. Nonsource interactions, such as with atmospheric ammonia, may

also occur, as indicated by additional results obtained in this study. Quantitative estimates, based on our results, of SO_2 to sulfate conversion in the atmosphere by gas-solid reactions indicate that the amount of conversion that occurs by this process will be primarily governed by aerosol burdens rather than SO_2 levels.

Initial deposition of SO_2 on ground-level surfaces was also found to be rapid. The surfaces investigated included selected soils and cements commonly found in urban environments. The cements, on average, were found to be more effective in removing SO_2 than the soils that were examined. The latter results indicate that certain construction materials widely used in urban areas may be helpful in removing atmospheric SO_2. Experimentally, we found that SO_2 deposition over both the soils and cements occurs by capacity-limited reactions, which indicates that these materials would lose their ability to remove SO_2 after prolonged environmental exposures. However, potential regenerative processes to rejuvenate surface activity may be operational in the environment. Laboratory experiments to examine these possibilities indicate that such processes do indeed exist.

In the case of H_2S and DMS deposition on ground-level surfaces, the experimental results indicate that these processes are not likely to be environmentally important. This conclusion, in turn, suggests possible long-range transport of these species in the environment, such that they could contribute to the sulfur-containing gas burden in urban atmospheres. However, results of work carried out in other laboratories (8-10) indicate that gas-phase oxidation of H_2S and DMS will limit their atmospheric lifetime to a few days or less.

SECTION 2

CONCLUSIONS

Results of laboratory investigation of interactions of sulfur dioxide (SO_2) and other sulfur-containing gases with solids representative of urban aerosols and environmental ground-level surfaces have indicated high initial reaction rates that gradually decrease with time (SO_2 exposure) owing to the observed capacity-limited nature of these reactions. Relative humidity was found to be very important in determining the capacity for, but not the rate of, SO_2 uptake. To within experimental error, the SO_2 was quantitatively converted to adsorbed sulfate over most of the solids studied. Atmospheric projections of these results indicated that SO_2 can be converted to sulfate at a rate as high as 32 percent/hr, with the reactions likely to be most important at or near emission sources. However, nonsource interactions with atmospheric ammonia could be important, as indicated by additional results obtained.

Studies of SO_2 deposition over selected soils and building surfaces yielded results qualitatively similar to those described above. Thus, initial reactivities were high but gradually diminished with SO_2 exposure; SO_2 removal was irreversible; and relative humidity had a significant effect on capacities for SO_2 uptake. Interestingly, various cements were found to be even more effective than soils for SO_2 removal. As in the case of SO_2 interactions with aerosol-like materials, we found that interaction with ammonia can be important in reactivating saturated surfaces. Additionally, precipitation washing away soluble surface reaction products was shown to be another potential surface reactivation process in the environment.

Results of studies of hydrogen sulfide (H_2S) and dimethylsulfide (DMS), biogenically emitted into the atmosphere in quantities comparable to anthropogenic SO_2 emissions, indicated that depositions of these species onto selected soils are not environmentally important.

SECTION 3

SO_2-AEROSOL INTERACTIONS

EXPERIMENTAL RESULTS

The detailed technical results of this study are given in Appendix A. The study involved laboratory measurements of the rates of reaction of SO_2 with solids likely to be found in urban aerosols. These included primarily metal oxides, selected on the basis of their abundance in urban aerosols and their likelihood to catalyze SO_2 oxidation, as well as fly ash from five different power plants. The latter, supplied in part by the Environmental Protection Agency (EPA), were from coal-fired plants (Appendix A).

Experiments were carried out in the tubular flow reactor illustrated in block diagram form in Figure 1. The reactor contained an inner, concentric cylinder that was coated with the solid of interest. As a gas mixture containing trace amounts of SO_2 passed through the reactor, the SO_2 diffused to the walls of the coated cylinder, where it was removed by heterogeneous reaction. This resulted in a decrease in SO_2 concentration as a function of distance down the tube. The SO_2 concentration gradient was measured by means of a system of small probes, whose intakes were centered along the cylinder axis, that were connected by means of a rotary valve to a mass spectrometer. Results from these experiments were analyzed in terms of ϕ-values or reactivities, which are approximately the fraction of SO_2-solid collisions leading to SO_2 removal. The measured ϕ-values were then used in conjunction with simple atmospheric models (11) to estimate SO_2 removal rates by SO_2-aerosol reactions under conditions representative of urban atmospheres.

Measured reactivities for freshly prepared solid coatings ranged from approximately 10^{-3} to less than 10^{-6} for the materials studied or from about 1 in 1000 SO_2-solid collisions being effective in removing SO_2 to less than 1 in 1,000,000. These results are given in Table 1 together with projected atmospheric removal rates for SO_2. The latter were calculated as described earlier (11), assuming that an atmospheric aerosol burden of 100 $\mu g/m^3$ had the same reactivity as the indicated solid, e.g., if 100 $\mu g/m^3$ of urban aerosol had the same reactivity as MgO, the SO_2 removal rate would be 32 percent/hr. Of course, urban aerosols would be composites of the materials given in Table 1, and many others, and actual

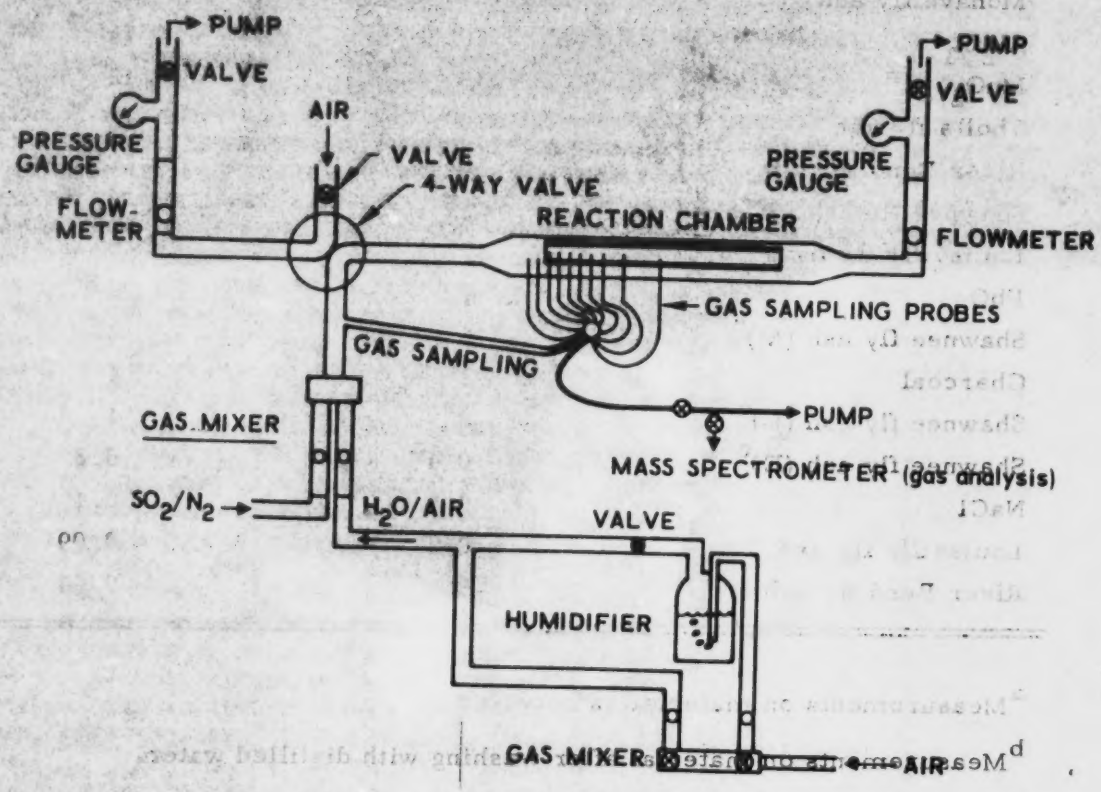

Figure 1. Tubular flow reactor.

TABLE 1. HETEROGENEOUS REMOVAL OF SO_2

Material	$10^5 \times \phi$	SO_2 removal (percent/hr)
MgO	100	35
Fe_2O_3	55	21
Mohave fly ash	50[a, b]	19
Al_2O_3	40	16
MnO_2	30	12
Cholla fly ash	30[a, b]	12
River Bend fly ash	30[b]	12
Shawnee fly ash (M)[c]	10[b]	4
Louisville fly ash	7[b]	3
PbO	7	3
Shawnee fly ash (M)[c]	5[a]	2
Charcoal	3	1
Shawnee fly ash (E)[c]	2[b]	1
Shawnee fly ash (E)[c]	0.4[a]	0.2
NaCl	0.3	0.1
Louisville fly ash	0.2	0.09
River Bend fly ash	<0.1[a]	<0.04

[a]Measurements on material as received.

[b]Measurements on material after washing with distilled water.

[c]From mechanical precipitator (M) or electrostatic precipitator (E).

removal rates would vary in proportion to the abundance of these materials in atmospheric aerosols. The type of study described here serves to identify the more reactive aerosol components.

Analysis of the surfaces after SO_2 exposure by x-ray photoelectron spectroscopy (ESCA) and wet chemical techniques indicated that, to within the accuracy of the methods employed (about a factor of 2), the SO_2 was quantitatively converted to adsorbed sulfate. An exception to this finding was seen for Al_2O_3, and possibly charcoal, where the experimental evidence indicated that SO_2 removal occurred by reversible physical adsorption, with little sulfate formation.

These removal rates are quite high and indicate the potential environmental importance of SO_2-aerosol reactions in SO_2 removal and, particularly, sulfate formation. However, we found that the high initial reactivities invariably decreased with time (SO_2 exposure) until, ultimately, the solids became totally unreactive toward SO_2 removal. This result indicates that the SO_2-solid reaction is a capacity-limited process. (In the case of the River Bend fly ash, ESCA analysis of the as-received material indicated an already high sulfate content. Washing the material with distilled water to remove soluble sulfates yielded the significantly enhanced reactivity given in Table 1.) Quantitatively, the solids investigated can remove from about 0.1 to greater than 50 percent of their weight of SO_2. Relative humidity was found to be very important in most cases in determining the amount of SO_2 that could be removed, with SO_2 removal increasing by up to two orders of magnitude, in some cases, with increasing humidity. The moisture content of the reaction mixture did not, however, affect the SO_2 removal rates to within experimental error.

The high initial reactivity, coupled with the limited capacity for SO_2 removal, indicates that freshly emitted aerosols will be active toward SO_2 for about 10 hr under typical urban conditions. In many instances, however (e.g., power plant stack emissions), SO_2 levels are much higher than those in the average urban atmosphere. Thus, at or near emission sources, aerosols may only be active for about 1 hr or less.

It has been suggested (1, 2, and references therein) that interaction of atmospheric ammonia with aerosols can be important in the heterogeneous oxidation of SO_2. This is believed to result from neutralization of sulfuric acid formed, which permits further reaction to occur. In order to examine this possibility, we exposed a Mohave fly ash sample to SO_2 until it would no longer remove this species. The sample was then sequentially exposed to ammonia and reexposed to SO_2. Results indicated that the reactivity of the fly ash to SO_2 removal was substantially restored (to about 50 percent of its original value).

ENVIRONMENTAL IMPLICATIONS

The results of these studies indicate the environmental importance of SO_2-aerosol reactions in particulate sulfate formation. The high initial oxidation rates observed indicate that these reactions can make an important contribution to secondary sulfate formation near emission sources. Beyond

the source region, the data indicate that their importance will diminish because of the capacity-limited nature of the reactions. However, interaction with atmospheric ammonia could promote further reaction in nonsource areas, as suggested by the experiment with Mohave fly ash rejuvenation by exposure to ammonia.

Measured capacities for SO_2 removal differed significantly from solid to solid and ranged from about 0.001 to 0.5 g SO_2 removed per gram of solid. The capacity of actual urban aerosols for SO_2 removal could have significant implications in control strategies for secondary sulfate formed by gas-solid interactions. For example, if capacities for SO_2 uptake were on the order of a few tenths of a gram of SO_2 removed per gram of solid (or less), present SO_2 and particulate levels (1) indicate that atmospheric sulfate originating from gas-solid interactions would be determined primarily by atmospheric aerosol levels. On the other hand, considerably higher capacities for SO_2 removal indicate that sulfate formation by this process would be controlled primarily by SO_2 levels. Our limited results support the former possibility.

An added result of interest in these studies is the significant increase in capacity for SO_2 uptake with increasing relative humidity. These results support suggestions (based in part on previous experimental work) that SO_2 oxidation in adsorbed water films, or water droplets, may well be one of the most important heterogeneous processes for SO_2 to sulfate conversion.

SECTION 4

INTERACTION OF SULFUR-CONTAINING GASES WITH GROUND-LEVEL SURFACES

EXPERIMENTAL RESULTS

The detailed technical descriptions of these laboratory studies are given in Appendices B and C. They were carried out in the tubular flow reactor used in the studies described in Section 3 and Appendix A. Data were analyzed in terms of the deposition velocity Vg, a pseudo-heterogeneous rate constant for removal of the species of interest at a ground-level surface. As indicated in Appendix B, the deposition velocity is the product of the reactivity ϕ, which was described in the preceding section, and the gas-solid collision frequency, which can readily be calculated from simple kinetic theory (12). The atmospheric flux of a trace species to an environmental surface can be determined by multiplying the deposition velocity of the trace species by its atmospheric concentration.

In the case of sulfur dioxide, we measured deposition velocities over selected soils as well as construction surfaces commonly found in urban environments. The results of these measurements are given in Table 2. The deposition velocities of SO_2 over soils, which agree well with other measurements (13), indicate that these materials are effective in the removal of atmospheric SO_2. In addition, it is seen from Table 2 that the cements investigated were even more effective than the soils for removing SO_2. The average deposition velocity for the soils was 0.71 cm/sec, compared with the average value for the cements of 1.8 cm/sec.

The removal of SO_2 was irreversible and was found to occur by capacity-limited reactions. Presumably, adsorbed sulfates were formed by surface reactions, although wet chemical analyses were largely unsuccessful because of interferences by various species present in the unexposed samples. Measured capacities for SO_2 removal from humidified reaction mixtures were in the range of 0.4-2.8 g SO_2 removed per square meter of surface. Capacities for removal from dry mixtures were factors of 3-10 lower, depending on the solid.

The possible rejuvenation of the reactivity of surfaces whose capacity for SO_2 uptake had been completely expended by prolonged exposure to SO_2 was also examined in these studies. Potential environmental rejuvenation mechanisms include precipitation washing away soluble surface reaction

TABLE 2. DEPOSITION OF SULFUR-CONTAINING GASES ONTO GROUND-LEVEL SURFACES

Surface[a]	Deposition velocity (cm/sec) SO_2	H_2S	DMS[b]
Cement (1)[c]	2.5		
Ready-mix cement[c]	2.0		
Exterior stucco (1)[c]	1.8		
Cement (2)[c]	1.6		
Adobe clay soil (1)	0.92	0.016	0.28
Exterior stucco (2)[c]	0.86		
Adobe clay soil (2)	0.66		
Sandy loam soil (1)	0.65		
Sandy loam soil (2)	0.60	0.015	0.064
Asphalt	0.04		

[a](1) and (2) refer to different material sources within the Los Angeles area.

[b]Dimethylsulfide.

[c]Cured.

products, restoring reactivity, and interaction with atmospheric ammonia. These possibilities were examined in the laboratory by exposing selected surfaces to SO_2 until they were no longer active in removing this species. The exposed surfaces were then rinsed with distilled water (to simulate rain washing away soluble surface reaction products, i.e., sulfates) or exposed to ammonia. When these surfaces were subsequently reexposed to SO_2, the reactivities were restored to those of the freshly prepared surfaces, which supported the ideas discussed above as viable environmental rejuvenation processes.

We also measured deposition velocities for H_2S and dimethylsulfide (DMS) over selected soil samples, as indicated in Table 2. Here the deposition velocities for DMS, and especially H_2S, were quite low compared with those observed for SO_2. Moreover, in the case of H_2S and DMS, we found that deposition occurred by means of reversible processes (presumably physical adsorption) and that irreversible removal processes occurred at rates at least a factor of 5 lower than those given in Table 2 for these two species. Our results indicate that deposition processes of H_2S and DMS onto ground-level surfaces do not appear to be environmentally important.

ENVIRONMENTAL IMPLICATIONS

The results for SO_2 deposition over selected soils and building materials indicate that these surfaces can be effective in the removal of atmospheric SO_2. Of particular interest are the results for SO_2 removal over various types of cements. Not only do the latter imply that such materials can be helpful in removing SO_2 from urban atmospheres, but they also indicate additional strategies that could be used for passive SO_2 control to complement emission source control measures.

Thus, specific concrete formulations in widespread use could be examined for SO_2 uptake rates to determine which are more effective in SO_2 removal. Design of exterior surfaces could be carried out in such a manner as to maximize available surface area for SO_2 removal. We suspect paint would be much less effective for SO_2 removal, indicating that these surfaces should not be painted. Sandblasting of older surfaces might also be helpful. Many of these criteria could be applied to interior surfaces as well. Designing interior surfaces to maximize SO_2 uptake would be particularly beneficial to individuals who may be especially sensitive to SO_2 exposure. Spedding et al. (14-17) have already done much work on SO_2 uptake by interior surfaces.

Of course, the capacity-limited nature of the SO_2 uptake indicates that additional measures would have to be considered. Experimentally, we found that the cements studied lose their ability to remove SO_2 when exposures reach the order of 1 g of SO_2 removed per square meter of surface in humidified gas mixtures. For an atmospheric SO_2 concentration of 50 $\mu g/m^3$ and a deposition velocity of 1.8 cm/sec, these results indicate that saturation would occur in approximately two weeks. (Actually, a somewhat longer period would be required because reactivity decreases with exposure, as indicated in Appendix B.) From our results on rejuvenation of activity by washing surfaces with water, a weekly hosing down of concrete surfaces in

a dry area such as Los Angeles in the summer might be an effective way of maintaining the activity of these surfaces for SO_2 removal. Natural precipitation could serve the same purpose in wetter parts of the country. Of course, care would have to be exercised in handling wash water in order to minimize sulfate pollution in runoff waters.

Although the results for H_2S and DMS deposition over selected soils indicate that these are not likely to be environmentally important processes, they also indicate the possibility of long-range transport of these species in the atmosphere. However, results of recent work (8-10) have indicated that both of these species can be readily oxidized by homogeneous reactions in the atmosphere that would limit their lifetime to about one day.

SECTION 5

PUBLICATIONS AND PRESENTATIONS

Publications, reports, and presentations that resulted from this work are given here. The first item listed in each section represents work carried out on our previous EPA grant (Grant No. 801340, Final Report No. EPA-650/3-74-007, August 1974) but reported on during the initial time period of this grant.

PUBLICATIONS

Stewart, T. B., and H. S. Judeikis. Measurements of Spatial Reactant and Product Concentrations in a Flow Reactor Using Laser-Induced Fluorescence. Rev. Sci. Instrum. 45:1542-1545, 1974.

Judeikis, H. S., and T. B. Stewart. Laboratory Measurement of SO_2 Deposition Velocities on Selected Building Materials and Soils. Atmos. Environ. 10:769, 1976.

Judeikis, H. S., and A. G. Wren. Deposition of H_2S and Dimethylsulfide on Selected Soil Materials. Accepted for publication, Atmos. Environ., May 1977.

Judeikis, H. S. Heterogeneous Reactions of Gaseous Air Pollutants. To be published, Calif. Air Environ. 1977.

Judeikis, H. S., T. B. Stewart, and A. G. Wren. Heterogeneous Removal of Atmospheric SO_2. Submitted for publication, Atmos. Environ. May 1977.

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Stewart, T. B., and H. S. Judeikis. Measurements of Spatial Reactant and Product Concentrations in a Flow Reactor Using Laser-Induced Fluorescence. ATR-74(7441)-1, The Aerospace Corp., 1 April 1974.

Judeikis, H. S., and T. B. Stewart. Laboratory Measurements of SO_2 Deposition Velocities. ATR-76(7498)-1, The Aerospace Corp., 19 February 1976.

Judeikis, H. S., and A. G. Wren. Deposition of H_2S and Dimethylsulfide on Selected Soil Materials. ATR-77(7498)-1, The Aerospace Corp., June 1977.

Judeikis, H. S., T. B. Stewart, A. G. Wren, and J. E. Foster. The Role of Solid-Gas Interactions in Air Pollution. ATR-77(7498)-2, The Aerospace Corp., 15 July 1977.

PRESENTATIONS

Stewart, T. B., S. Siegel, H. S. Judeikis, and H. R. Hedgpeth. Reaction of NO_x on Particle Surfaces. American Chemical Society, 167th National Meeting, Los Angeles, 31 March-5 April 1974.

Judeikis, H. S. Heterogeneous Removal of SO_2 From the Atmosphere. 8th Aerosol Technology Meeting, University of North Carolina, Chapel Hill, North Carolina, 6-8 October 1975.

Judeikis, H. S. Heterogeneous Removal of SO_2 From the Atmosphere. Workshop on the Chemistry of Atmospheric Sulfur, Drexel University, Philadelphia, 12-14 October 1976.

Judeikis, H. S. Heterogeneous Reactions of Gaseous Air Pollutants, SO_2, NO_x, Freon Derived Species. California Institute of Technology, Environmental Engineering Science Seminar, 23 February 1977.

Judeikis, H. S. Heterogeneous Removal of SO_2 From the Atmosphere. American Chemical Society, 173rd National Meeting, New Orleans, 20-25 March 1977.

Judeikis, H. S. Heterogeneous Reactions of Sulfur- and Nitrogen-Containing Pollutant Gases. Particulate Pollutant Workshop, University of California, Riverside, 21-22 April 1977.

Judeikis, H. S. Heterogeneous Reactions of Gaseous Air Pollutants. Gordon Conference on Chemistry at Interfaces, Meriden, New Hampshire, 18-22 July 1977.

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APPENDIX A

LABORATORY STUDIES OF HETEROGENEOUS REACTIONS OF SO_2

INTRODUCTION

Interest in gas-aerosol reactions in the atmosphere stems from a need to understand such reactions and their impact on atmospheric chemistry, as well as their contribution to atmospheric haze formation and health effects attributable to aerosols in the respirable size range. Of particular current interest are heterogeneous reactions of SO_2 and the contribution of these reactions to atmospheric sulfate aerosol burdens [Environmental Protection Agency (1975)]. Potential heterogeneous processes for SO_2 to sulfate conversion, involving solid and liquid aerosols, have recently been reviewed [Environmental Protection Agency (1975), Hidy and Burton (1975), and Brock and Durham (1977)].

Reactions between gaseous SO_2 and solids have been investigated for years, since these reactions are used extensively in the industrial production of sulfuric acid, the leading chemical commodity. The data gleaned from these studies, however, are of limited use in predicting atmospheric conversion rates because of the high temperatures and reactant pressures used in industrial processes.

In the past decade, laboratory studies conducted under conditions more nearly approximating those of the ambient atmosphere have demonstrated the potential importance of SO_2-solid reactions to sulfate aerosol burdens. Examples of this work include that of Okita (1967) and Urone et al. (1968), who found that SO_2 removal from gas mixtures was accelerated in the presence of selected solids that are of atmospheric interest. Similar results were obtained by Smith, Wagman, and Fish (1969), who used a novel exploding wire technique to generate aerosol particles, and by workers at the University of Pittsburgh [Cheng, Frohliger, and Corn (1971); Cheng, Corn, and Frohliger (1971); and Corn and Cheng (1972)], who used a flow reactor in which aerosol particles were suspended on Teflon beads. Chun and Quon (1973) studied the oxidation of SO_2 on ferric oxide particles, whereas Okita (1967); Devitofrancesco, Panke, and Petronio (1972); and Burke, Baker, and Moyers (1973) observed SO_2 removal by collected atmospheric particles. Some of these studies demonstrated the capacity-limited nature of SO_2 uptake, attributed to a lowering of the surface pH by sulfuric acid formation [e.g., Junge and

Ryan (1958), Van den Heuvel and Mason (1963), Scott and Hobbs (1967), Foster (1969), and McKay (1971)].

A number of studies have also been carried out, by various experimental techniques, to identify adsorbed sulfur compounds. Examples include measurements by x-ray photoelectron spectroscopy (ESCA or XPS) conducted by Novakov, Chang, and Harker (1974) and Barbaray, Contour, and Mouvier (1977). Electron paramagnetic resonance spectroscopy has been used extensively by Lunsford and co-workers, as well as others [Lin and Lunsford (1975) and references therein]. Many measurements have also been made with infrared spectroscopic techniques [e.g., Goodsel, Low, and Takezawa (1972); Lin and Lunsford (1975); and references therein].

A number of the earlier studies yielded only minimum rates for SO_2 uptake and sulfate formation, because measurements were limited by gas-phase diffusion to the solid surface or by the detection of SO_2 in the effluent from a laboratory reactor. In most of the latter cases, SO_2 was detected in the effluent stream only after partial saturation of the solid surface; consequently, initial reaction rates could not be determined. Moreover, only a few of the earlier studies reported on capacities for SO_2 removal.

In this work, we report on the rates and capacities of heterogeneous reactions of SO_2 with a number of solids likely to be found in urban aerosols. The rates were measured in the laboratory by means of a cylindrical flow reactor in which the walls were coated with the solid of interest. This type of configuration permitted us to measure initial rates as well as rates as a function of time (SO_2 exposure). Analysis of the experimental results specificially accounts for mass transport in the reactor, yielding rates that depend only on the surface processes responsible for SO_2 uptake.

These results indicate that SO_2 uptake, in most cases, occurs through capacity-limited reactions that convert SO_2 to adsorbed sulfate. Initial uptake rates are quite high. With time, however, the measured rates decrease until, with prolonged exposure to SO_2, the solids completely lose the ability to remove this species from the gas stream. Quantitative projections of these results to the atmosphere, by use of a model previously described [Judeikis and Siegel (1973)], indicate that SO_2-aerosol reactions are likely to be most important at or near the emission source and that, after a short time ($\sim$ 1 hr) in the atmosphere, they will lose their ability to remove SO_2. However, interaction with atmospheric ammonia could promote further reaction, as discussed under Results.

We find that the relative humidity of the gas mixture is important in the SO_2 reaction scheme. Although moisture does not alter reaction rates appreciably for SO_2 uptake, in most cases SO_2 capacities increase significantly with increasing relative humidity. The results obtained with humidified reaction mixtures indicate that reactions taking place in adsorbed surface water films may well be one of the most important factors in SO_2 uptake and adsorbed sulfate production in aerosols.

EXPERIMENTAL

A detailed description of the apparatus used in these experiments can be found elsewhere [Judeikis and Stewart (1976)]. The apparatus was a flow reactor consisting of two concentric Pyrex cylinders, the inner one coated with the solid of interest. The leading 15 cm of the inner cylinder was left uncoated in order to permit full development of laminar flow. A homogeneous gas-phase mixture containing trace amounts of the SO_2 was allowed to flow through the reactor, where this species could diffuse to the walls for removal by heterogeneous reaction. This led to both axial (flow direction) and radial concentration gradients for the trace species. The axial concentration gradient was measured with a mass spectrometer, coupled to the cylinder by means of a multiport rotary valve, and a series of small (0.15-cm o.d.) probes whose intakes were centered along the axis of the inner cylinder. The results were analyzed by use of a model that specifically accounted for mass transport by diffusion and laminar flow [Judeikis and Stewart (1976)]. The analysis yielded heterogeneous reactivities in terms of ϕ-values, the fraction of SO_2-solid collisions that are effective in removing SO_2. Runs were also done on blank (uncoated) cylinders; these gave no indication of reaction between SO_2 and the cylinder walls ($\phi < 10^{-7}$).

The coated cylinders were generally prepared from water-ethanol (1:1) slurries of the appropriate solid, except for several fly ash samples (the Shawnee and Louisville ashes described in the following paragraph) that were prepared with water as the slurry medium. In addition, several samples of MnO_2 were saturated with dilute acid or base solutions before being prepared as water-ethanol slurries. The slurries were deposited onto the Pyrex cylinder and the coated cylinders allowed to air dry. They were subsequently vacuum-dried at 10^{-4} Torr overnight in the reactor.

Except for fly ash samples, all gases, liquids, and solids used in these studies, whether for sample preparation, experiments, or analyses, were reagent grade materials. Two different forms of aluminum oxide were used: Al_2O_3 and a mixed oxide Al_2O_3-Al(OH)O. These materials gave similar results, which are combined herein under Al_2O_3. The fly ash samples, all from coal-fired plants and supplied in part by the EPA, were from the Mohave power plant on the Colorado River near Hoover Dam, the Cholla power plant in Arizona, the River Bend power plant at Charlotte, North Carolina, the Shawnee steam plant at Paducah, Kentucky, and Combustion Engineering Louisville Gas and Electric, Louisville, Kentucky. Ashes from the Shawnee facility were obtained from both mechanical and electrostatic precipitators.

Typical operating conditions used in the experiments included pressures from 10-700 Torr, flow velocities of 1-30 $cm^3\ s^{-1}$ (average linear velocities of 0.05-1.5 $cm\ s^{-1}$), and ambient temperatures (Reynolds numbers < 50). Depending upon the reactivity of SO_2 toward a particular surface, subambient pressures were often required to measure nondiffusion-limited reactivities [Judeikis and Stewart (1976)]. The concentration of SO_2 was varied from 3-100 ppm, with occasional excursions up to 1000 ppm; the mass spectrometer sensitivity toward SO_2 detection was ~ 0.3 ppm. Oxygen concentrations were varied from 0-10 percent. Higher oxygen concentrations could not be used since they led to oxidation of the ionization filament in the mass spectrometer.

In several experiments, Mohave fly ash samples were exposed sequentially to SO_2, NH_3, and SO_2. The ammonia exposures were done with gaseous NH_3. On occasion, the ammonia exposures interfered with the operation of the reactor, possibly because of NH_3 adsorption on tubing, valves, etc. In such instances, purging the system with NO_2 completely eradicated the deleterious effects.

Selected solids were analyzed for their BET surface areas [Brunauer, Emmett, and Teller (1938)] so that capacities for reaction could be related to the solid's active surface area. These types of measurements are well known, and an apparatus was built based upon the design found in a familiar physical chemistry laboratory text [Shoemaker and Garland (1967)]. These BET surface areas can be found in Table A-1.

Wet-chemical analyses for sulfate were performed on metal oxide samples after exposure to SO_2. The procedure involved removing the exposed, coated cylinder from the reactor, separating the solid from the cylinder, washing the solid with distilled water, and analyzing the wash water for soluble sulfate. Analyses were carried out by precipitating barium sulfate from the wash water by adding a dilute barium chloride-nitric acid solution. Nitric acid was required to prevent coprecipitation of carbonate ion; an excess of nitric acid was avoided in order to reduce the probability of dissolving the barium sulfate.

In addition to the wet chemical analysis, selected SO_2-exposed metal oxides and fly ashes were examined by means of x-ray photoelectron spectroscopy (ESCA). Two instruments were used. MnO_2 and fly ash samples were analyzed on a Du Pont 650 B electron spectrometer that used a magnesium x-ray source and was operated at about 350 watts. Quoted instrument resolution at the time of the experiment was 1.05 eV FWHM on an Au_{4f} (7/2) peak. These samples were prepared by dusting the powdered oxides on double-sided tape. The experiments were performed on three samples of each substance; one sample was a blank, and the other two had been exposed to SO_2 in the reactor. The second ESCA instrument was a GCA/McPherson ESCA 36 photoelectron spectrometer equipped with a cryopump that allowed pressures of 10^{-9} Torr to be attained. This spectrometer also used a magnesium anode that emitted K_α x-rays at an energy of 1253.6 eV. Resolution of this instrument was 0.2 eV. Various samples of the metal oxides were prepared on glass slides by the method that was used in preparation of the flow tube samples. The coated slides were exposed to SO_2 in the tubular reactor. After exposure, samples were carried in air to the ESCA and analyzed in the usual manner. Metal oxides and salts examined this way included MnO_2, $MnSO_4$, MgO, $MgSO_4$, Fe_2O_3, $Fe_2(SO_4)_3$, Al_2O_3, $Al_2(SO_4)_3$, Na_2SO_3, and combinations of these substances such as $Al_2(SO_4)$ and Al_2O_3. All binding energies were referenced to the C_{1s} peak in order to compensate for charging effects.

TABLE A-1. HETEROGENEOUS REMOVAL OF SO_2 OVER VARIOUS MATERIALS

Material	BET surface area[a] ($m^2 g^{-1}$)	$10^5 \times \phi$[b]	SO_2 removal (percent/hr^{-1})
MgO		100	35
Fe_2O_3	27.3	55	21
Mohave fly ash	15.2[c]	50[c,d]	19
Al_2O_3	215	40	16
MnO_3	109	30	12
Cholla fly ash		30[c,d]	12
River Bend fly ash		30[d]	12
Shawnee fly ash (M)[e,f]		10[d]	4
Louisville fly ash[f]		7[d]	3
PbO		7	3
Shawnee fly ash (M)[e,f]		5[c]	2
Charcoal	40.7	3	1
Shawnee fly ash (E)[e,f]		2[d]	1
Shawnee fly ash (E)[e,f]		0.4[c]	0.2
NaCl		0.3	0.1
Louisville fly ash[f]		0.2[c]	0.09
River Bend fly ash		< 0.1[c]	< 0.04

[a]Uncertainties are ±5 percent.

[b]Uncertainties are ±30 percent.

[c]Measurements on material as received.

[d]Measurements on material after washing with distilled water.

[e]From mechanical precipitator (M) or electrostatic precipitator (E).

[f]Here only, one sample.

RESULTS

Results from a representative experiment for SO_2 removal over Mohave fly ash are shown in Figure A-1. The triangles represent the experimentally measured SO_2 concentration gradient. The solid curve was calculated from the laminar flow model [Judeikis and Stewart (1976)] for a best-fit reactivity (ϕ-value) of 4.4×10^{-4}, which represents the fraction of gas-solid collisions that were effective in removing SO_2. Reactivities determined in this manner for a number of different solids are listed in Table A-1, together with several measured BET surface areas and projected atmospheric removal rates for SO_2 (the latter are discussed in the following section). The reactivities in Table A-1 are averages of initial values determined for the most part from five or more separate samples. Uncertainties in reactivities (standard deviations) are ~30 percent and result primarily from variation in SO_2 uptake from sample to sample.

The reactivities given in Table A-1 were found to be independent of SO_2 and O_2 concentrations, as well as relative humidity and total pressure to within a factor of 2. Representative data illustrating this point are shown in Table A-2. These data were obtained on sequential runs on the same samples in order to minimize sample-to-sample variations in reactivities. Thus, the data indicate that heterogeneous removal of SO_2 occurs through first-order or psuedo-first-order kinetics.

Reactivities were also found to be independent of the thickness of the solid coatings used in these experiments. For example, MnO_2 coatings with average thicknesses of 0.48, 0.96, 8.1, and 64 μm all gave the same initial reactivity to within 20 percent. These results indicate that only the outer layer of particles in the film are effective in SO_2 removal since particle diameters, as determined by scanning electron microscopy, ranged from a few tenths of a micrometer to ~0.5 μm.

The results discussed thus far are for freshly prepared solid coatings. With continued exposure to SO_2, reactivities gradually diminish until, with prolonged exposures, the solids become unreactive toward removal of SO_2. This effect is illustrated in Figure A-2 for SO_2 removal over MnO_2, where the reactivity relative to the initial reactivity ϕ_o is plotted as a function of time (SO_2 exposure). Similar effects were found for all of the materials investigated.

Experiments such as that illustrated in Figure A-2 gave additional evidence that only the outermost layer of particles were involved in SO_2 removal. The data in Figure A-2 are for an MnO_2 coating with an average thickness of 0.48 μm. Data from an experiment conducted under virtually identical conditions, except with an average film thickness of 8.1 μm, are essentially superimposable on those illustrated in Figure A-2.

Results such as those in Figure A-2 indicate SO_2 removal occurs through capacity-limited reactions. Capacities for SO_2 removal can be determined from such experiments by measuring total SO_2 uptake. Results for various solids are given in Table A-3. It will be noted that, particularly for MgO and MnO_2, capacities increase significantly with relative humidity.

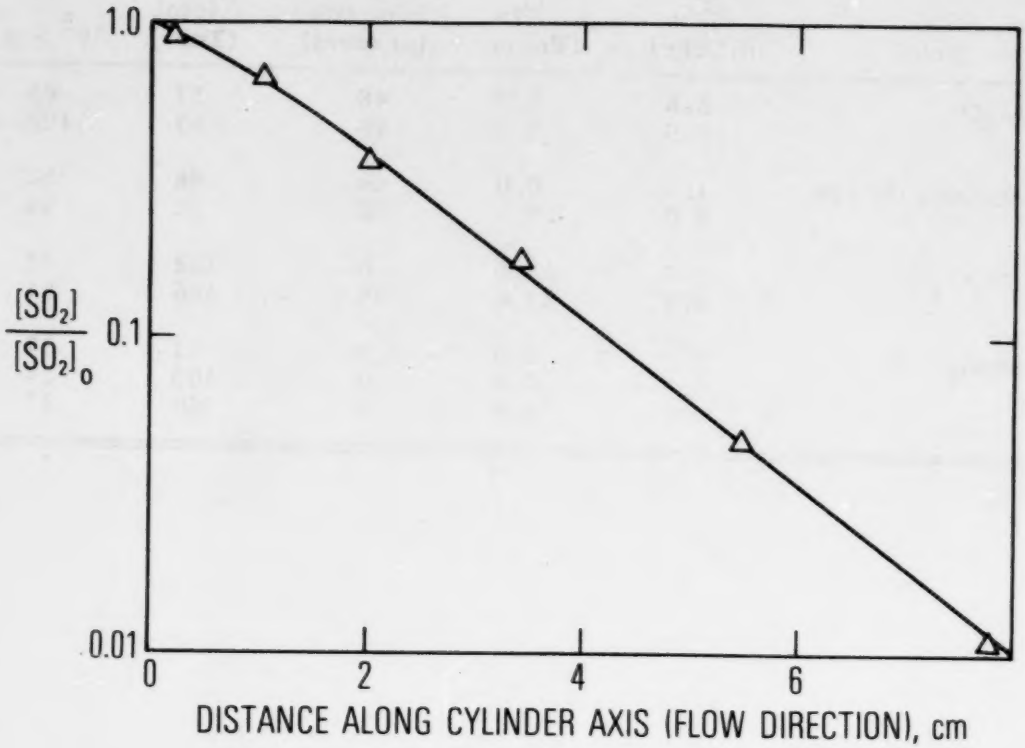

Figure A-1. Removal of SO_2 by Mohave fly ash. Triangles represent experimentally measured SO_2 concentrations. Solid curve was calculated from the laminar flow model for $\phi = 4.4 \times 10^4$. Experimental conditions: total pressure, 55 Torr; O_2 pressure, 6 Torr; partial pressure of SO_2 in the influent gas stream, 9 mTorr; relative humidity, 0 percent.

TABLE A-2. EFFECTS OF SO_2, O_2, RELATIVE HUMIDITY, AND TOTAL PRESSURE ON SO_2 REMOVAL RATES

Solid	P_{SO_2} (mTorr)	P_{O_2} (Torr)	Relative humidity (percent)	P_{total} (Torr)	$10^5 \times \phi$
MgO	2.6	5.7	48	57	95
	19.5	5.9	48	59	102
Mohave fly ash	1.6	0.0	48	48	52
	2.0	4.9	52	52	54
Fe_2O_3	4.0	11.0	0	102	42
	3.9	11.0	95	106	51
MnO_2	9.5	0.0	0	51	27
	6.4	0.0	0	103	24
	9.0	0.0	0	300	27

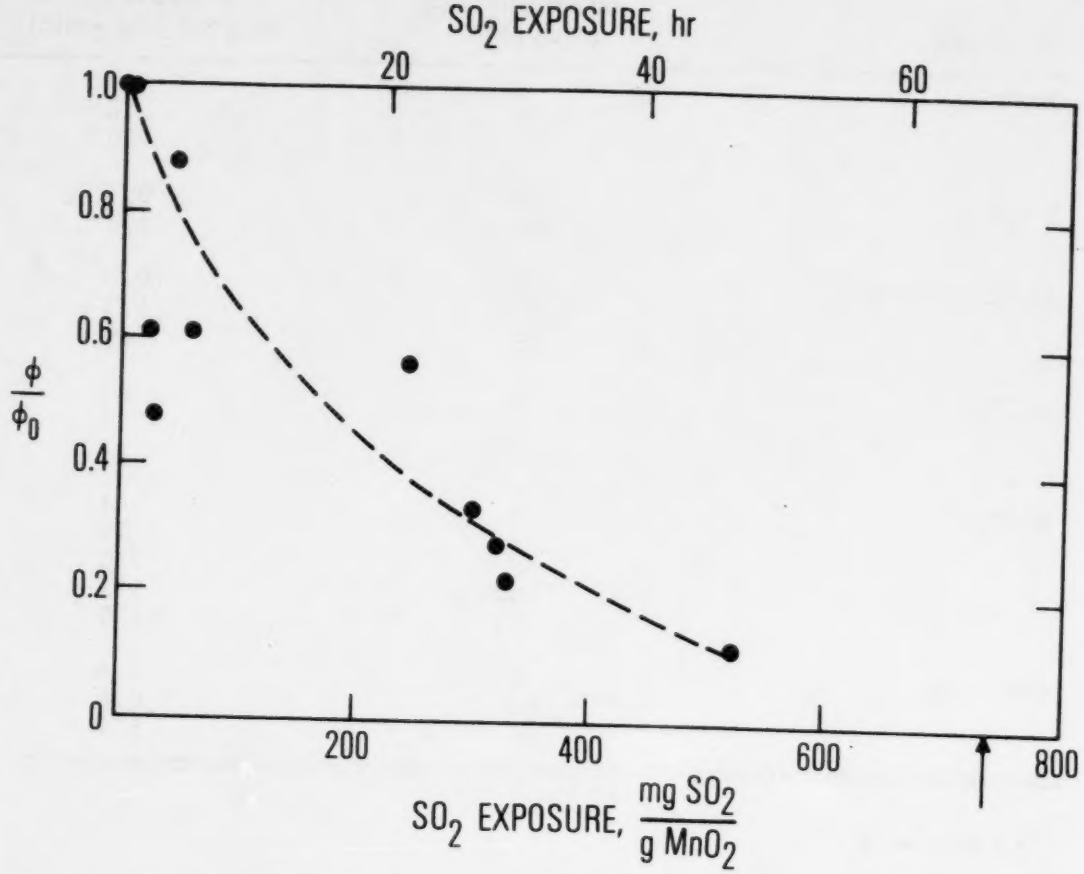

Figure A-2. Reactivity as a function of SO_2 exposure for SO_2 removal over MnO_2. SO_2 in nitrogen, 95-percent relative humidity. The arrow indicates the stoichiometric point for the reaction $MnO_2 + SO_2 \rightarrow MnSO_4$.

TABLE A-3. CAPACITIES FOR SO_2 REMOVAL

Solid	Relative humidity (percent)	Capacity[b] (mg SO_2) (g solid)$^{-1}$
MgO	0	4
	50	12
	95	400
Fe_2O_3	0	0.6
	50	1.2
Mohave fly ash[a]	0	0.5
	50	0.2
	95	1.4
Al_2O_3	0	25
	53	5
	95	17
MnO_2	0	4
	25	78
	58	320
	50-95	210
	95	>530
Charcoal	0	1.3
	56	0.8
	95	5.7

[a]As received.

[b]Probably minimum values (see text).

This contrasts to reactivities that did not change, to within experimental error, with relative humidity. However, capacities, like reactivities, were found to be independent of SO_2 and O_2 concentrations, as well as total pressure. The latter conclusions for capacities are based on a more limited number of experiments.

Quantitatively, we can combine the capacity data in Table A-3 with the BET surface areas in Table A-1 in order to determine the surface coverage of these materials by SO_2. For the materials in Table A-3, except MgO and MnO_2, this amounts to ~0.03-0.2 monolayer, if absorbed SO_2 is assumed to occupy 15Å^2. For MnO_2 at 0-percent relative humidity, we find a comparable value of 0.05 monolayer. However, in the latter case, coverage increases substantially with increasing relative humidity and is about seven monolayers at 95-percent relative humidity. Similar conclusions probably also apply for MgO, although we have not measured the BET surface area of this material.

The capacities and surface coverages given in Table A-3 and the preceding paragraph are based on the total weight of solids used in the experiments. As such, they are probably minimum values, since capacity experiments were generally carried out with coatings that consisted of multiparticle layers. As noted above, the experimental evidence indicates that only the outermost layer of particles participates in SO_2 removal. Capacities and surface coverages, therefore, are probably an order of magnitude greater than those given above.

Wet chemical and ESCA analyses of these materials indicate SO_2 is quantitatively (to within a factor of 2) converted to adsorbed sulfate. (Because of the broad nature of the ESCA sulfate peak, we would not have been able to detect a 5-10-percent contribution by sulfite or similar species.) One exception to this result was the case of Al_2O_3 (and possibly charcoal), where both types of analyses indicated that little, if any, sulfate was formed. Further, the ESCA analyses revealed no detectable amounts of any sulfur-containing species. The latter results indicate that SO_2 uptake on Al_2O_3 occurred by reversible physical adsorption, the SO_2 desorbing during the evacuation to 10^{-9} Torr prior to ESCA analysis. This interpretation is consistent with results from the flow reactor, where we found that the reactivity of Al_2O_3 exposed to SO_2 until saturated could be restored by evacuating the sample at 10^{-4} for ~1 hr. The latter did not occur to any appreciable extent for the other materials in Table A-1, except for charcoal.

The capacity-limited nature of the reaction, accompanied, in most cases, by sulfate formation, suggested the possibility that the fly ash materials as received may already have undergone substantial reaction with SO_2. Indeed, ESCA analysis of the Mohave fly ash, as received, indicated a strong sulfate signal. For this reason, we examined the fly ash materials both as received and after they had been washed with distilled water for removal of soluble sulfates. As indicated in Table A-1, in most cases the washing led to substantial increases in the fly ash reactivity.

In addition to washing materials with distilled water, we also examined the effects of pretreatment with dilute acids or bases, since it has been

suggested that ammonia plays an important role in the heterogeneous oxidation of SO_2, primarily through neutralization of H_2SO_4 [Junge and Ryan (1958), Van den Heuvel and Mason (1963), Scott and Hobbs (1967), and McKay (1971)]. We pretreated MnO_2 with a dilute NH_4OH solution (0.1 N), as well as 0.1 N solutions of NaOH, HCl, and H_2SO_4. The results of these studies, illustrated in Table A-4, indicate that the basic pretreatments substantially accelerate initial reactivities toward SO_2 removal, whereas the acidic pretreatments have the opposite effect.

TABLE A-4. EFFECT OF BASIC AND ACIDIC TREATMENT OF MnO_2 ON INITIAL SO_2 REMOVAL RATES

Pretreatment[a]	P_{SO_2} (mTorr)	P_{O_2} (Torr)	Relative humidity (percent)	P_{total} (Torr)	$10^5 \times \phi$
NH_4OH	0.9	0	0	51	240
NaOH	17.0	1.4	50	59	85
None	1.1	0	0	50	30
HCl	1.3	0	0	50	5
H_2SO_4	0.8	0	0	51	2

[a] MnO_2 films prepared from distilled water slurries or 0.1 N solutions of base or acid.

In the case of the Mohave fly ash, we conducted an experiment to test the possible rejuvenation of reactivity of spent material by exposure to ammonia. In that experiment, the Mohave ash was exposed to SO_2 until it was totally nonreactive toward this species. The SO_2 exposure was then terminated and the sample exposed to ammonia (total ammonia exposure on a molar basis was <10 percent of the SO_2 exposure required to poison the ash). The material was then reexposed to SO_2 with the result that the reactivity was restored to ~50 percent of its initial value.

DISCUSSION

The results in Table A-1 indicate that a number of materials exhibit substantial reactivity toward SO_2. These reactivities may be used to estimate atmospheric removal rates of SO_2 through gas-aerosol reactions. Here we use a previously derived model for gas-aerosol reactions [Judeikis and Siegel (1973)], wherein the SO_2 removal rate is given by

$$-\frac{d(SO_2)_a}{dt} = \phi k_c (A)(SO_2)_a \qquad \text{(A-1)}$$

In Eq. (A-1), k_c is the average SO_2 velocity in one dimension; (A), the aerosol surface area per unit volume; $(SO_2)_a$, the atmospheric sulfur dioxide concentration, and ϕ, the fraction of SO_2-aerosol collisions that are effective in removing SO_2. The value of (A) can be calculated from an expression given by Mottershead (1970) or by integration of actual aerosol distributions [e.g., Heisler, Friedlander, and Husar (1973)], if particles are assumed to be spherical. In either case, for an atmospheric aerosol loading of 100 $\mu g\ m^{-3}$, we estimate (A) $\approx 1.5 \times 10^{-5}\ cm^2\ cm^{-3}$. Using this value, and k_c calculated from simple kinetic theory [Present (1958)], we obtain

$$\frac{-d \ln(SO_2)_a}{dt} = 0.12\ \phi\ sec^{-1} \qquad (A\text{-}2)$$

From Eq. (A-2) and the ϕ-values in Table A-1, we obtained the projected atmospheric removal rates given in the last column of Table A-1. It should be noted that calculation of these rates was based on the assumption that the total atmospheric aerosol burden had the same reactivity as the indicated solid. Thus, for example, if the total atmospheric aerosol burden had the same reactivity as MgO, the SO_2 removal rate would be 35 percent/hr^{-1}.

The above calculations estimate SO_2 removal rates based on simple kinetic theory, i.e., treatment of aerosol particles as large molecules. Although this is appropriate for small aerosol particles ($<\sim 0.01\ \mu m$), it overestimates rates for larger particles because of a transition from free-molecular flow to aerodynamic flow [Hidy and Brock (1970) and Fuchs and Sutugin (1971)]. Using approximations for mass transfer given in the latter references, and integrating over the aerosol distribution used above [Heisler, Friedlander, and Husar (1973)], we estimate that these effects could reduce the projected SO_2 removal rates given in Table A-1 by approximately a factor of 2.

In addition, the capacity-limited nature of the removal process indicates that these reactions will be most important at or near the emission source. If we assume that $\phi \rightarrow 0$ as the SO_2 exposure approaches 0.1 g of SO_2 removed per gram of solid, and a linear relationship between ϕ and the SO_2 removed, we may write

$$\phi = \phi_o \left[1 - 10 \frac{(SO_2)_r}{(P)}\right] \qquad (A\text{-}3)$$

where ϕ_o is the initial reactivity and $(SO_2)_r$ and (P) are the concentrations (in $\mu g\ m^{-3}$) of SO_2 removed and particles, respectively. If we let $\phi_o = 1 \times 10^{-4}$ and (P) = 100 $\mu g\ m^{-3}$, Eq. (A-3) becomes

$$\phi = 1 \times 10^{-4} \left[1 - 0.1(SO_2)_r\right] \qquad (A\text{-}4)$$

But the rate of SO_2 removal from Eq. (A-2) is

$$-\frac{d(SO_2)_a}{dt} = \frac{d(SO_2)_r}{dt} = 430\ \phi\ (SO_2)_a\ hr^{-1} \qquad (A\text{-}5)$$

for a particle loading of 100 $\mu g\ m^{-3}$, where $(SO_2)_a$ is the atmospheric concentration of SO_2, which we shall take as 50 $\mu g\ m^{-3}$. Substituting the latter value and Eq. (A-4) into Eq. (A-5) and integrating yield

$$(SO_2)_r = 10(1 - e^{-0.22t})\ \mu g\ m^{-3} \qquad \text{(A-6)}$$

[Note that substitution of Eq. (A-6) into Eq. (A-3) would give the exponential type of decay in ϕ/ϕ_o indicated in Figure A-2.] Substitution of t = 1, 3, and 10 hr into Eq. (A-6) gives $(SO_2)_r$ = 2.8, 4.8, and 8.9 $\mu g\ m^{-3}$, respectively. Thus, since $(SO_2)_r \rightarrow 10\ \mu g\ m^{-3}$ as $t \rightarrow \infty$, fresh aerosols would lose 90 percent of their activity toward removing SO_2 from the ambient urban environment in only ~ 10 hr.

At emission sources, however, SO_2 loadings can typically be an order of magnitude or more greater than those in the surrounding urban environment [Newman, Forrest, and Manowitz (1975a, 1975b)]. Under these conditions, most of the heterogenous interactions would take place on a time scale of ~ 1 hr. Thus, the results of this study indicate that heterogeneous removal of SO_2 (and conversion to sulfate) will occur primarily at, or near, emission sources, in agreement with other recent conclusions [e.g., Foster (1969); Newman, Forrest, and Manowitz (1975a, 1975b); Freiberg (1976); and Lusis and Phillips (1977)]. However, the possibility for further reaction exists as ambient air begins to mix with the plume from the source. The latter conclusion is based on the experimental results involving the rejuvenation of the reactivity of expended Mohave fly ash after exposure to ammonia, an event that would occur on mixing of ambient air with an emission plume.

The significant increases in capacities found at higher relative humidities for selected solids in these studies indicate that reactions taking place in adsorbed water films are likely to be of primary importance in atmospheric SO_2-solid interactions. Additionally, although sulfate aerosol production by gas-phase processes and reactions in liquid droplets can occur, the results of these studies indicate that contributions to atmospheric sulfate burdens by gas-solid reactions will be limited by atmospheric particle burdens rather than SO_2 concentrations. This is the result of the capacity-limited nature of the reactions, which, considering atmospheric SO_2 and aerosol burdens, indicates that only a fraction of the gaseous SO_2 in the atmosphere can be converted to sulfate by these processes. This conclusion could have a serious impact on source emission control strategies.

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APPENDIX B

LABORATORY MEASUREMENT OF SO_2 DEPOSITION VELOCITIES ON SELECTED BUILDING MATERIALS AND SOILS

INTRODUCTION

Deposition velocities of pollutant gases are used extensively in calculating atmospheric budgets for these species [e.g., Robinson and Robbins (1970) and Kellogg et al. (1972)]. Both field and laboratory measurements of these quantities have been made. Field measurements generally employ one of two methods for determination of deposition velocities. The first involves simultaneous measurements of wind velocity, temperature, and pollutant gas concentration profiles above the surface [e.g., Garland et al. (1973, 1974); Shepherd (1974); Dannevik, Frisella, and Fishman (1974); and Whelpdale and Shaw (1974)]. The vertical atmospheric diffusity K(z) is estimated from the former two quantities, and the deposition velocities V_g calculated from

$$F = -K(z)\frac{dc}{dz} = V_g\, c \qquad \text{(B-1)}$$

relating the downward flux (F) of the pollutant gas to K(z) and the concentration gradient. In Eq. (B-1), it is assumed that the downward flux of the pollutant gas may be treated as diffusive transfer. The concentration c [actually $\lim_{z\to 0} c(z)$] is generally measured at some fixed height above (but near) the surface.

The second method, which is also used extensively in the laboratory, is based on total uptake of SO_2 [Braun and Wilson (1970); Seim (1970); Hill (1971); Abeles et al. (1971); and Cox and Penkett (1972)], frequently employing ^{35}S labeled SO_2 [Spedding et al. (1969a, 1970a, 1970b, 1971, 1972a, 1972b); and Owers and Powell (1974)]. In the latter case, the total uptake of $^{35}SO_2$ is measured, as well as its concentration just above the surface. The deposition velocity is then readily calculated from Eq. (B-1). In some cases, flow systems are also used for laboratory measurements [Chamberlain (1966); Spedding (1969b, 1972c); Brimblecombe and Spedding (1972); and Payrissat and Bielke (1975)].

Measured deposition velocities typically range from a few tenths of a centimeter per second or less to several centimeters per second [e.g., Spedding (1972b)]. Substantial variations in the magnitude of the deposition

velocity determined at a given field site or for a given material in the laboratory are common [Garland et al. (1973, 1974); Shepherd (1974); and Whelpdale and Shaw (1974)]. These variations may be related in part to the failure of the assumptions inherent in Eq. (B-1) as well as to surface changes that are dependent on environmental conditions. For example, SO_2 uptake by leaves is controlled largely by the stomata [Meidner and Mansfield (1968)]. The opening and closing of the stomata depend on a number of environmental factors such as daylight, relative humidity, and season. In the laboratory, deposition velocities have been found to depend on the degree of gas phase mixing employed in static systems [Spedding (1972b)] and on gas flow rates in dynamic systems [Lawrence (1964) and Spedding (1972c)], the measured deposition velocities increasing with higher degrees of mixing or flow rates.

The latter results indicate that measured deposition velocities, in many cases, represent values that are limited by mass transport to the surface. Questions then arise as to the limits of deposition velocities imposed by physical and chemical processes related to the actual removal of the pollutant gas at the surface.

In this work, we present a method for laboratory measurement of deposition velocities independent of mass transport phenomena, together with experimental results for SO_2 removal on several environmental surfaces. The values obtained in this manner represent the maximum deposition velocities that would be encountered in the open atmosphere, particularly when turbulent mixing is sufficiently high to remove mass transport limitations.

EXPERIMENTAL

Apparatus

A block diagram of the apparatus used in these experiments is illustrated in Figure B-1. This system, which is basically a cylindrical flow reactor, is similar to systems previously described [Hedgpeth et al. (1974) and Stewart and Judeikis (1974)]. The major difference between the present system and the ones previously described is the method of analyzing gases flowing through the reactor. In addition, system components that were found to be reactive toward SO_2 were replaced. Virtually all components in the final version of the modified system consisted of Pyrex glass, 316 stainless steel, and Teflon-coated aluminum.

In the system shown in Figure B-1, a carrier gas stream was initially split into two streams; one of the streams passed through a humidifer, where it was saturated with water vapor, and the two streams were subsequently recombined. (The ratio of flow rates of the split streams determined the relative humidity of the carrier gas.) The carrier gas stream was then mixed with a small amount of nitrogen that contained traces of SO_2, and the mixture was fed into the cylindrical flow reactor (2.5-cm radius) that contained a concentric Pyrex cylinder (2.1-cm radius) coated with the solid of interest. (The choice of a cylinder for a substrate was not unique, and other geometrics, such as parallel plates, could have been used.) The latter

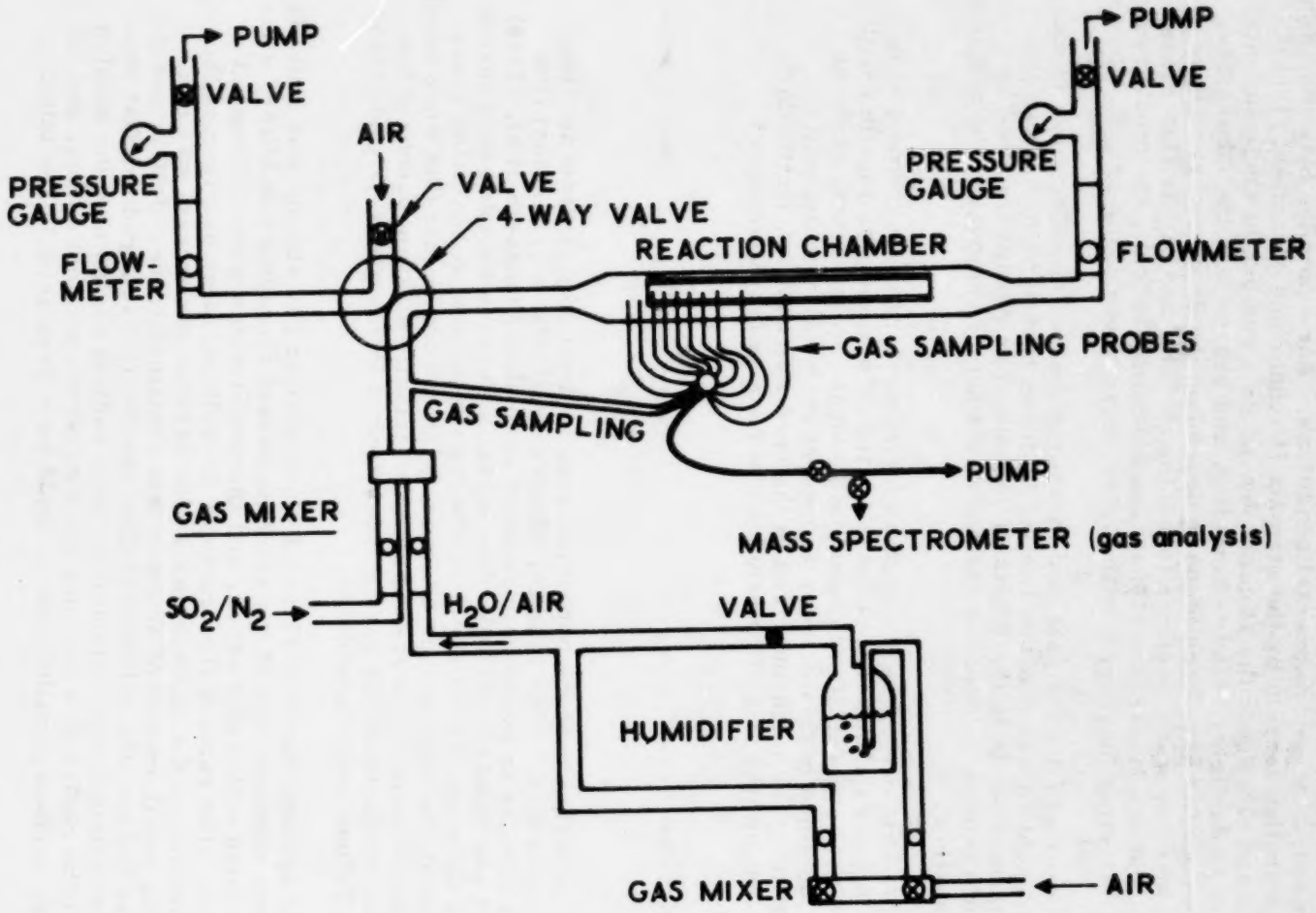

Figure B-1. Block diagram of cylindrical reactor.

cylinder was coated by preparing a slurry of the solid of interest, coating the blank Pyrex cylinder (outside the reactor), and permitting the coating to air dry and then dry overnight in vacuum in the tubular reactor. Surface roughnesses of the dried films were typically $\lesssim \sim 1$ mm.

Reaction of SO_2 with the coated walls led to a concentration gradient for SO_2 along the axial (as well as radial) directions. (In the absence of a solid coating, there was no change in the SO_2 concentration on passage through the reactor.) For measurement of the axial concentration gradient, the gas mixture in the reaction chamber was sampled by means of a set of small probes (connected by a 16-port rotary valve to a mass spectrometer), whose intakes were centered along the axis of the coated cylinder. The outside and inside diameters of the probes were nominally 0.15- and 0.08-cm, respectively. Flow through the sampling system was sufficiently slow that the flow pattern in the reaction chamber was essentially undisturbed [Westenberg, Raezer, and Fristrom (1957)], yet sufficiently fast that transit time through the sampling system was minimal ($\sim$ 3-4 sec).

Typical operating conditions employed were pressures of 10-700 Torr, flow velocities of 1-30 cm^3/sec (average linear velocities of 0.05-1.5 cm/sec), and ambient temperatures (Reynolds numbers < 50). Subambient pressures were frequently required to measure nondiffusion-limited deposition velocities. (This point is discussed more fully in subsequent sections of this appendix.) The flow rates chosen gave a sufficiently high axial SO_2 concentration gradient to permit accurate measurements of this quantity.

Gases sampled by means of the probes were analyzed with a mass spectrometer. The 0.15-cm-o.d. tubing continued into the mass spectrometer chamber, terminating just before the ionizer. Thus, effluent gases from the probe were injected directly into the ionizer. The sensitivity of the mass spectrometer for SO_2 detection was $\sim$ 0.3 ppm. Consequently, experiments were conducted with initial SO_2 concentrations ≥ 3 ppm. In addition, high concentrations of oxygen in the reaction mixture tended to oxidize the filaments in the mass spectrometer. For this reason, oxygen concentrations were limited to $\sim$ 10 percent or less.

Materials

Solids examined in this study consisted of commercial formulations of cement, ready-mix cement (cement containing sand and gravel), asphalt, and exterior stucco. In the case of cement and exterior stucco, samples from two different sources of each material were used. Soil samples of sandy loam and adobe clay taken from the Los Angeles area were also examined. In most cases, these materials were sifted through a screen in order to eliminate particles > 1 mm in diameter. Water-based slurries of these materials were employed in preparing the coated Pyrex cylinders (except for asphalt, where a trichloroethylene slurry was used). Consequently, the cement, ready-mix cement, and exterior stucco were cured during the process of preparing the coatings. Surface roughnesses were typically $\lesssim \sim 1$ mm.

Gases used in this study were reagent grade gases obtained from Matheson and were used as received. Two specially prepared mixtures were used for SO_2 and oxygen in order to achieve the desired concentrations of these gases in the reaction mixture. These were 1000-ppm SO_2 in N_2 and 20-percent O_2 in N_2. In addition, distilled water was used for humidifying gas mixtures.

Data Analysis

Mass transport in a cylindrical flow tube, under conditions of non-turbulent flow and at steady state, is described by [e.g., Walker (1961), Stewart and Judeikis (1974), and references therein]

$$D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2}\right) - V_x \frac{\partial c}{\partial x} = 0 \qquad \text{(B-2)}$$

subject to the boundary conditions

$$c = c_0 \text{ at } r,\ x = 0 \qquad \text{(B-3)}$$

$$\frac{\partial c}{\partial r} = 0 \text{ at } r = 0,\ x \qquad \text{(B-4)}$$

and

$$-D\frac{\partial c}{\partial r} = \phi k_r c \text{ at } r = R,\ x > 0 \qquad \text{(B-5)}$$

In Eqs. (B-2) through (B-5), r and x are the radial and axial coordinates; c is the concentration of the reacting species (initial concentration of c_0); D is the diffusion coefficient of the reacting gas in the mixture; V_x is the linear gas flow velocity in the axial direction; k_r ($= \sqrt{\mathcal{R}T/2\pi M}$, where $\mathcal{R}$, T, and M are the gas constant, absolute temperature, and molecular weight of the diffusing gas, respectively) is the molecular velocity of the reacting species in the radial direction; and R is the cylinder radius. [Throughout this report, binary diffusion coefficients were calculated for SO_2 in nitrogen by the use of expressions given by Present (1958). The presence of oxygen or water vapor in the reaction mixture would lead to diffusion coefficients slightly different than the calculated values. The uncertainties arising from these differences are less than the uncertainties arising from other sources.]

Equation (B-5) expresses the condition that the diffusion of the reacting species to the walls is equal to its removal by heterogeneous reaction. In that equation, $k_r c$ is the gas-solid collision frequency, and the reactivity ϕ, a dimensionless parameter, is the fraction of collisions that lead to removal

of the reacting species from the gas phase.[1] Actually c', the concentration at one mean free path away from the walls, should be used in Eq. (B-5) in place of c [Paneth and Herzfeld (1937) and Stewart and Judeikis (1974)]. However, except for $\phi \approx 1$, the two are essentially equal.

The deposition velocity V_g is related to ϕ as can be seen by comparing Eqs. (B-1) and (B-5). Equating the right-hand sides of those equations yields the result

$$V_g = \phi k_r \tag{B-6}$$

Thus, the deposition velocity over a given material can be obtained from laboratory determinations of ϕ-values. Note also that the deposition velocities determined in this fashion correspond to values at one mean free path above the surface.

Solution of Eq. (B-2) is generally accomplished by making several simplifying assumptions. One of these is the assumption of plug flow

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[1] For first-order or psuedo-first-order processes, ϕ is actually composed of a collection of constants, including the sticking coefficient, as well as the rate constants for adsorption, desorption, and surface reaction. Consider, for example, a reaction scheme involving first-order adsorption, desorption, and surface reaction processes. Equation (B-5) would then be rewritten as

$$- D \frac{\partial c}{\partial r} = k_a c - k_d c_a = \gamma(1 - f) k_r c - k_d c_a$$

where k_a and k_d are the rate constants for adsorption and desorption, c_a is the concentration of adsorbed c, and γ and f are the sticking coefficient and fractional surface coverage, respectively. If we assume a steady state for c_a, we may write

$$\frac{dc_a}{dt} = \gamma(1 - f) k_r c - k_d c_a - k_s c_a = 0$$

where $k_s c_a$ is the rate of surface reaction of adsorbed c. Solving the latter equation for c_a and substituting the result into the former equation, we find

$$- D \frac{\partial c}{\partial r} = \gamma(1 - f) \left(\frac{k_s}{k_d + k_s} \right) k_r c$$

Comparison of this expression with Eq. (B-5) indicates that for the case discussed here

$$\phi = \gamma(1 - f) \left(\frac{k_s}{k_d + k_s} \right)$$

(V_x = constant). The solution in this case is [e.g., Walker (1961), Stewart and Judeikis (1974), and references therein]

$$\frac{c}{c_0} = \sum_{i=1}^{\infty} \frac{2J_0\alpha_i \frac{r}{R}}{\alpha_i\left(1 + \delta^2\alpha_i^2\right) J_1(\alpha_i)} e^{\beta_i x} \tag{B-7}$$

where $J_0(\alpha_i \frac{r}{R})$ and $J_1(\alpha_i)$ are Bessel functions of the first kind

$$\delta = \frac{D}{Rk_r\phi} \tag{B-8}$$

$$\beta_i = \frac{V_x}{2D}\left\{1 - \sqrt{\left[1 + \left(\frac{D\alpha_i}{RV_x}\right)^2\right]}\right\} \tag{B-9}$$

and α_i is the i^{th} root of

$$J_0(\alpha_i) = \delta\alpha_i J_1(\alpha_i) \tag{B-10}$$

In the case of laminar flow [$V_x = 2V_{average}(1 - r^2/R^2)$], solutions to Eq. (B-2) have been obtained [for equivalent heat transfer problems by Sideman, Luss, and Peck (1965) and references therein] where axial diffusion can be neglected [$D(\partial^2 c/\partial_x 2) \approx 0$]. [Criteria necessary for this assumption were delineated in an analogous heat transfer problem by Singh (1958)]. In general, we find that the conditions for which these solutions apply in our experiments are of limited usc in the determination of values for ϕ. The reason for this is that reactions tend to become diffusion limited under experimental conditions where axial diffusion can be neglected, particularly for high reactivities. Examples of this point are illustrated below. Consequently, numerical solutions of Eq. (B-2), with laminar flow, were required for the cases of interest here. These were obtained by using a modification of the method of finite differences [Jenson and Jeffreys (1963)].

The geometry of our system is such that laminar flow is not fully developed at the entry to the coated cylinder. [Laminar flow is fully developed after entry to the reaction chamber. However, the flow pattern is disrupted when the gas stream encounters the leading edge of the coated cylinder (Figure B-1). For our typical operating conditions, several centimeters would be required for laminar flow to be reestablished (Betz (1966)]. This generally presents no problem, however, since we find that, under most experimental conditions, either the plug or laminar flow models adequately describe our experimental results (in fact, in many cases, concentration profiles calculated from either model are indistinguishable) and yield ϕ-values that agree to within a few to 20 percent. (Values derived from the plug flow model are <u>always</u> lower than those derived from the laminar flow model.)

The major discrepancy between ϕ-values derived from the two models occurs at high pressures ($\sim$ 700 Torr) and high reactivities ($\phi > 10^{-4}$). Under these conditions, SO_2 removal tends to become diffusion limited. Although these conditions are avoided in most experiments (see below), they do provide an opportunity to distinguish between the two models (since the solutions become independent of ϕ). In such cases, we generally find that SO_2 concentration gradients calculated from the plug flow model are more consistent with experimentally measured values. Consequently, the plug flow model was used for the analysis of data reported here. As noted above, any deviations from this model would result in slightly higher values for ϕ (or V_g) than are reported below, by anywhere from a few to 20 percent.

In practice, data were analyzed by one of two methods. The first consisted of comparing experimental SO_2 concentration gradients to those calculated from Eq. (B-7) for the given experimental conditions and various values of ϕ until the best fit was obtained. The second, shorter method made use of the fact that only the first term in Eq. (B-7) contributes to the concentration at large axial distances [Stewart and Judeikis (1974)]. Thus, the SO_2 concentration gradient becomes exponential for large x. In this case, the limiting exponential slope from the experimental concentration profile was compared to those calculated from the first term of Eq. (B-7) for the given experimental conditions and various ϕ-values until the best fit was obtained.

RESULTS

Values of ϕ derived from a number of measurements of SO_2 removal over various solids are given in Table B-1, together with deposition velocities calculated from Eq. (B-1) for a temperature of 25°C. The values reported in Table B-1 represent averages from three to six experiments on each material investigated. (Each experiment was conducted with a fresh sample of the given material.) In the case of cement and exterior stucco, data on the material from different sources are reported individually.

The ϕ-values determined from consecutive measurements of SO_2 concentration gradients on a given sample usually agreed to within 20-30 percent. There were comparable variations in ϕ-values from sample to sample of the same material (for an equivalent SO_2 exposure, where exposure is defined as the time-integrated quantity of SO_2 to which the solid was exposed). (The effects of SO_2 exposure are discussed below.) Overall, the standard deviations for the values reported in Table B-1 are about 40 percent.

The values reported in Table B-1 were generally found to be independent of SO_2 concentrations over variations of one to two orders of magnitude. (The minimum partial pressure of SO_2 used in these experiments was $\sim$ 0.15 mTorr.) Representative data illustrating this point are shown in A of Table B-2 for exterior stucco-I. (Here, as in the other data presented in Table B-2, the comparisons were made in sequential runs on the same sample of a given material in order to minimize uncertainties arising from sample variations.) Thus, SO_2 removal over freshly prepared samples of these solids follows apparent or psuedo-first-order kinetics.

TABLE B-1. EXPERIMENTAL RESULTS FOR SO_2 REMOVAL

Material	ϕ	Vg (cm/sec)
Cement-I[a]	3.2×10^{-4}	2.5
Ready-mix cement[a]	2.6×10^{-4}	2.0
Exterior stucco-I[a]	2.3×10^{-4}	1.8
Cement-II[a]	2.0×10^{-4}	1.6
Exterior stucco-II[a]	1.1×10^{-4}	0.86
Adobe clay soil	8.4×10^{-5}	0.66
Sandy loam soil	8.3×10^{-5}	0.65
Asphalt	5.1×10^{-6}	0.04

[a]Cured.

Reactivities as a function of oxygen concentration and relative humidity were also examined, and ϕ was found to be independent of these parameters to within experimental error. In Table B-2, representative results from these experiments over ready-mix cement and sandy loam soil are presented in B and C, respectively. In the case of oxygen, problems with oxidation of the mass spectrometer filaments limited the oxygen concentrations used to $\lesssim$ 10 percent. However, even with those limitations, the oxygen concentration exceeded that of SO_2 by factors ranging from $\sim 10^3$ to 10^4 (except, of course, for experiments conducted in the absence of oxygen).

For materials exhibiting reactivities of $\sim 10^{-4}$ or greater, measurements made at atmospheric pressure yielded SO_2 concentration gradients approaching the diffusion-limited value. Consequently, values derived from such measurements were subject to large uncertainties. To illustrate this point, we show several concentration profiles that were calculated from our model for typical experimental conditions at atmospheric pressure. It will be seen that a reactivity $\geq 10^{-3}$ results in a diffusion-limited SO_2 concentration gradient, whereas the gradient for $\phi = 10^{-4}$ differs by only 10 percent from the diffusion-limited gradient.

The large uncertainties resulting from experiments conducted near the diffusion limit were avoided by altering the experimental conditions for those materials that exhibited reactivities approaching 10^{-4}. In principle, several parameters could be varied; in practice, however, the total pressure was the most sensitive and the most easily varied parameter. The effects of reducing the total pressure can be seen by comparing Figures B-2(a) and B-2(b). In the latter case (for 0.1-atm total pressure), the concentration gradients differ by approximately a factor of 2 for reactivities of 10^{-3} and 10^{-4}.

TABLE B-2. REACTIVITIES AS A FUNCTION OF SO_2 AND O_2 CONCENTRATIONS, RELATIVE HUMIDITY, AND TOTAL PRESSURE[a]

	Parameter varied	Material	Pressure, Torr			Relative humidity (percent)	ϕ
			Total	O_2	$SO_2 \cdot 10^3$		
A.	SO_2 concentration	Exterior stucco-I[b]	55	2.6	1.1	28	2.4×10^{-4}
			55	2.6	13.2	28	2.2×10^{-4}
B.	O_2 concentration	Ready-mix cement[b]	58	0.0	1.6	57	2.0×10^{-4}
			58	6.2	1.6	57	2.4×10^{-4}
C.	Relative humidity	Sandy loam soil	100	4.4	3.7	0	6.1×10^{-5}
			100	4.3	4.2	100	5.9×10^{-5}
D.	Total pressure	Sandy loam soil	50	0.0	4.2	50	8.3×10^{-5}
			400	0.0	4.8	50	7.4×10^{-5}

[a]Flow rates in all of these experiments were nominally 10 cm^3/sec.

[b]Cured.

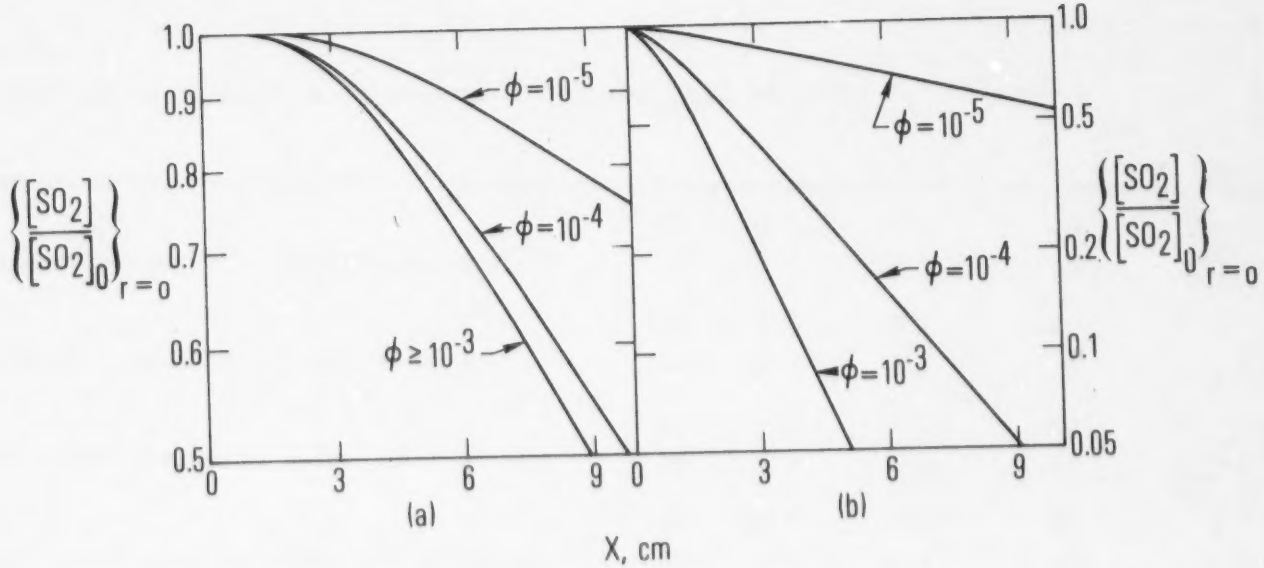

Figure B-2. Calculated SO_2 concentration gradients. Gradients calculated for total pressures of (a) 1.0 and (b) 0.1 atm. In both cases, R = 2.1 cm, T = 25° C, and V_x = 1 cm/sec.

Since subambient pressures were frequently used in these experiments, the effects of total pressure on measured reactivities were examined. In general, the ϕ-values were independent of total pressure, to within experimental uncertainties, for pressures ranging from $\sim$ 50-500 Torr. This point is illustrated for SO_2 removal over sandy loam soil in D of Table B-2.

An attempt was also made to analyze solids after reaction for sulfate formed. Wet chemical methods were employed. These attempts were largely unsuccessful because of interferences by various species present in the unexposed samples. However, in a related study on SO_2 removal by metal oxides and other materials (to be reported later), wet chemical and photoelectron spectroscopy methods indicate a near quantitative conversion of SO_2 to sulfate. [Seim (1970) obtained similar results upon exposing various soils to SO_2.]

The reactivities and deposition velocities reported above are for SO_2 removal over freshly prepared coatings. With time (SO_2 exposure), these reactivities diminish as the capacity to remove SO_2 is expended. This saturation effect is illustrated in Figure B-3 for adobe clay soil. In general, this type of behavior was found with all of the solids investigated in this study.

The capacities for SO_2 removal (total SO_2 removed from the initial exposure until complete saturation) can be determined from experiments such as that illustrated in Figure B-3. Values measured for several of the solids listed in Table B-1 (the adobe clay and sandy loam soils, ready-mix cement, and exterior stucco-I) range from 0.04-0.6 g SO_2/m^2 of solid surface for dry reaction mixtures and from 0.4-2.8 g SO_2/m^2 of solid surface for humidified reaction mixtures (50-95-percent relative humidity). Typically, we found that capacities for humidified reaction mixtures were a factor of 3-10 higher than those for dry mixtures. The number of experiments conducted to measure capacities is not sufficient for an accurate determination of the relationship between the capacity and relative humidity. The limited data do indicate, however, that the capacity for SO_2 removal from humidified reaction mixtures does not depend on relative humidity as long as the latter is $\geq \sim$ 30-40 percent. Other than the relative humidity, parameters such as the SO_2 and O_2 concentrations and the total pressure did not appear to have any significant effect on capacities for SO_2 uptake.

Although the experimental results suggest only a limited capacity for SO_2 removal by the ground-level surfaces examined here, several possibilities exist for continued removal in the open atmosphere. For example, rain could wash away soluble surfaces (or other products), rejuvenating the surfaces for further SO_2 uptake [Braun and Wilson (1970) and references therein]. Several authors [Spedding (1972b) and Payrissat and Beilke (1975)] have suggested that SO_2 removal may be pH limited (e.g., sulfuric acid is formed from SO_2 taken up by the surface, with the reaction gradually decreasing as the acid concentration builds up). Interaction with atmospheric ammonia could diminish such an effect. Of course, sulfates are nutrients for plant growth, and sulfates formed on soils could be removed by this process.

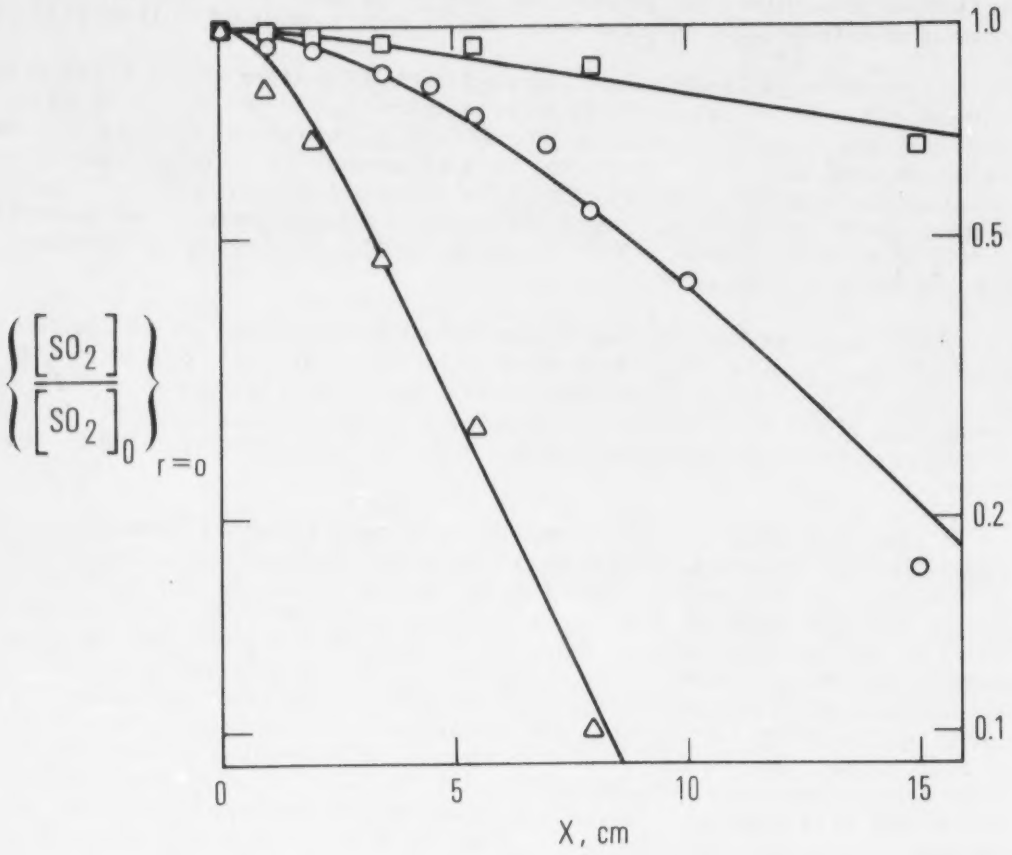

Figure B-3. Measured SO_2 concentration gradients as a function of time (SO_2 exposure). Experimental parameters for SO_2 removal over adobe clay soil: P(total) = 300 Torr; $P(O_2)$ = 19 Torr; $P(SO_2)$ = 22 mTorr; T = 24° C; V_x = 0 5 cm/sec. Gradients after exposures to SO_2 of 3.6 min (–△–), 2.7 hr (–O–), and 7.7 hr (– □ –), or 0.009, 0.39, and 1.1 g SO_2/m^2 of solid surface, respectively. Data points are from experimental measurements. Solid curves are calculated for ϕ = 1.0 × 10-4 (–△–), 1.2 × 10^{-5} (–O–), and 2.2 × 10^{-6} (– □ –).

Several additional experiments were carried out in order to examine these possibilities. In one experiment, a sample of ready-mix cement was exposed to SO_2 at 95-percent relative humidity until the capacity of this material for SO_2 removal was completely expended. (In general, we found that SO_2 removal was an irreversible process. Thus, termination of SO_2 exposures and evacuation of solid samples did not lead to any desorption of SO_2 or restoration of the ability of the solid to remove SO_2.) The coated cylinder was then removed from the reactor, and the coating was rinsed with distilled water and allowed to air dry. The coated cylinder was then replaced into the reactor, dried overnight in a vacuum, and subsequently reexposed to SO_2 at 95-percent relative humidity. Experimental measurements indicated a complete restoration of the ability of ready-mix cement to remove SO_2 (e.g., to within the experimental uncertainties noted above, the ready-mix cement exhibited the same reactivity as a freshly prepared, previously unexposed sample).

In another experiment, adobe clay soil was exposed to SO_2 in a dry reaction mixture until completely saturated. The gas mixture was then humidified (95-percent relative humidity), and, again, the reactivity toward SO_2 removal was completely restored.

The effects of ammonia were examined in an experiment with a sample sandy loam soil. The sample was exposed to SO_2 (95-percent relative humidity) until completely saturated. The SO_2 exposure was then terminated, and the sample was exposed to NH_3 (the total NH_3 exposure was only ~ 20 percent of the SO_2 exposure required to initially saturate the sample). Following the exposure to ammonia, the system was purged with nitrogen and then reexposed to SO_2. The result, again, was a complete restoration of the activity of the sandy loam soil toward SO_2 removal.

DISCUSSION

In the analysis of data obtained from these experiments, we specifically account for transport-related phenomena. Thus, the deposition velocities given in Table B-1 represent values that are limited only by the adsorption and chemical processes leading to SO_2 removal from the gas phase. These values, then, represent the maximum deposition velocities that would be encountered over the materials listed in Table B-1 under turbulent atmospheric conditions.

Experimentally, for materials with reactivities $> 10^{-4}$, such as exterior stucco or cement, we found it necessary to conduct experiments at subambient pressures in order to obtain nondiffusion-limited reactivities. Although such conditions deviate from the ambient atmosphere, the results are more applicable than would be results obtained from experiments conducted at atmospheric pressures. The reason for this is that diffusivities for SO_2 in our experiments, which are conducted under nonturbulent conditions, are ~ 0.1 cm^2/sec at atmospheric pressure [Fish and Durham (1971)]. Generally, however, turbulent atmospheric eddys are consideredably higher than this, by factors of $\sim 10^3$-10^5 [Csanady (1973) and Heines and Peters (1974)]. Thus,

a process that would be diffusion limited in our laboratory experiments would more likely be limited by the adsorption and chemical processes responsible for uptake than by transport to the surface in the open atmosphere, particularly under turbulent conditions.

Of course, a viscous sublayer, whose thickness depends on a number of environmental factors (e.g., surface roughness), exists near the surface where diffusivity approaches molecular diffusion [Csanady (1973)]. As the thickness of this boundry layer increases, the SO_2 uptake will tend to become more diffusion limited. Thus, the actual deposition velocities in the environment will range from the maximum values reported here in turbulent atmospheres to those determined by molecular diffusion in quiet atmospheres.

An added feature of the type of experiment reported herein is the ability to measure changes in deposition velocities with time (SO_2 exposure). In a number of measurements reported in the literature, materials are exposed for a fixed period of time and total SO_2 uptake determined. Such measurements can only give an average value for the deposition velocity, the magnitude of which will depend upon the degree of saturation of the solid under study.

It is instructive to compare our results with other data reported in the literature for related materials. In a study conducted on seven European soils in a system in which a fan was used to mix the air above the soil, Payrissat and Beilke (1975) reported deposition velocities of 0.19-0.60 cm/sec. These authors also observed first-order kinetics for SO_2 removal, saw evidence of saturation, and measured a slight dependence of removal rates on relative humidity. In an additional study on five soils from the midwestern United States, Seim (1970) measured average deposition velocities of 0.2 cm/sec. He also found that deposition velocities were relatively independent of SO_2 concentrations (first-order kinetics) and moisture levels.

Measurements of deposition velocities over building materials, notably limestone, have been reported in the literature [Spedding (1969a, 1969b) and Braun and Wilson (1970)]. Reported values are in the range of 0.03-0.3 cm/sec, which are considerably lower than the values we find for cements and stuccos. These differences may result, in part, from differences in the materials used and, in part, from values derived from diffusion-limited experiments in some of the earlier work. However, Braun and Wilson (1970) obtained values of 2.4-2.6 g/m^2 for the sulfur content of limestone exposed to atmospheric SO_2; these values compare favorably with the higher capacities for SO_2 uptake we have measured in humidified reaction mixtures.

Several interesting possibilities are indicated by the deposition velocities and capacities for SO_2 uptake measured here and in other laboratories. If we assume an average deposition velocity of 1 cm/sec and an atmospheric SO_2 concentration of 0.1 ppm, from Eq. (B-1), we calculate a deposition rate of 2.6×10^{-6} g/m^2 sec. If we further assume a capacity of 2.5 g SO_2/m^2 of solid surface, we conclude that the ability of a solid surface to remove SO_2 from the atmosphere will be expended in 11 days, in the absence of any

processes such as precipitation that might act to rejuvenate the surface activity for SO_2 removal. In an urban area such as Los Angeles, where midsummer precipitation is negligible, this could result in higher SO_2 concentrations than would otherwise be experienced. Of course, this type of calculation and conclusion is greatly oversimplified for a number of reasons.

Other variables enter into application of the data in Table B-1 to the environment, such as surface roughness and total areas as well as source strengths. In general, our samples had surface roughnesses $\leq \sim 1$ mm. Surface roughnesses in the environment are usually greater than this, in some cases by large factors. In the environment, therefore, the actual surface area available for uptake could be significantly greater than that available in our reactor. Of course, vegetation would have a very high ratio of actual to ground-level surface areas; however, as noted above, the uptake by vegetation, which is largely controlled by the stomata, would be sensitive to environmental factors [Meidner and Mansfield (1968)].

In addition, we indicated several possibilities above for rejuvenating saturated surfaces. The few experiments we conducted to explore these possibilities supported those suggestions. Thus, in the atmosphere, uptake of SO_2 may be determined by the balance of rates of saturation and rejuvenation of the active surface.

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APPENDIX C

DEPOSITION OF H_2S AND DIMETHYLSULFIDE ON SELECTED SOIL MATERIALS

INTRODUCTION

A knowledge of deposition rates of trace gases onto ground-level surfaces is essential to calculating atmospheric budgets for these species as well as their transport in the environment. The interest in sulfur-containing species over the past two decades has prompted a number of measurements of deposition of oxidized sulfur-containing species over a wide variety of ground-level surfaces [e.g., Judeikis and Stewart (1976) and references therein]. However, little is known of the deposition of reduced sulfur compounds. Significant quantities of the latter species ($\sim$90-280 Tg S yr^{-1}) result from biogenic emissions in the environment, as inferred from analyses of the global sulfur cycle [Friend (1973) and references therein].

Originally, it was thought that biogenic sulfur emissions were composed primarily of H_2S. Some recent studies indicate significant contributions of organic sulfides, such as dimethylsulfide (DMS), to the biogenic sulfur emissions [Lovelock, Maggs, and Rasmussen (1972) and Rasmussen (1974)]. On the basis of seawater measurements, laboratory experiments, and qualitative conclusions regarding the fate of H_2S in oxidizing fresh and ocean surface waters, the latter authors suggest that organic sulfur compounds may dominate biogenic sulfur emissions. Liss and Slater (1974), however, estimate a biogenic flux of DMS from ocean surfaces of 3.7 Tg S yr^{-1}. Similarly, Hitchcock (1975, 1976) concludes that DMS emissions can contribute only $\sim$2-5 Tg S yr^{-1} to biogenic sulfur emissions. She also cites the work of Chen and Morris (1972) on the aqueous oxidation of sulfide to conclude that H_2S is the dominant form of biogenic sulfur emissions, in agreement with earlier suggestions. Both H_2S and DMS have been detected in field measurements in the United States. Natusch et al. (1972) measured H_2S concentrations of $\sim$0.05 ppb in Colorado. Maroulis and Bandy (1977) found similar levels of DMS on the Atlantic Coast, although lower levels, typically $<$ 0.03 ppb, were found at a site near Norfolk, Virginia.

Here we report on the laboratory measurement of the velocities of H_2S and DMS deposition over selected soil samples. We find that the measured deposition velocities for these species are lower, in some cases by almost

two orders of magnitude, than those observed for SO_2 deposition over the same materials. These and other considerations discussed herein lead us to conclude that dry deposition of H_2S and DMS cannot be important processes in the environment.

EXPERIMENTAL

The apparatus and procedures used in these experiments have been described elsewhere [Judeikis and Stewart (1976)]. The apparatus consisted of a cylindrical flow reactor in which the walls of an inner concentric cylinder were coated with the material of interest. As a homogeneous gas-phase mixture containing trace amounts of the reagent gas of interest flowed through the cylinder, the trace species diffused to the walls where it was removed by deposition on the solid surface. This resulted in concentration gradients for the trace species along the cylinder axis (flow direction) as well as the radial dimension. The axial concentration gradient was measured by means of a system of small probes whose intakes were centered along the cylinder axis. These probes were coupled, by means of a multiport rotary valve, to a mass spectrometer. The model used in the analysis of data from these experiments specifically accounted for mass transport by diffusion and flow. For determination of the deposition velocity, use was made of the boundary condition (at the inner cylinder wall)

$$-D \frac{\partial c}{\partial r} = V_g c$$

that equates the diffusive flux of the trace species to the wall with its heterogeneous removal rate, where D is the (molecular) diffusivity of the trace species in the gas mixture, c and $\partial c/\partial r$ its concentration and radial concentration gradient at the wall, and V_g the deposition velocity [Judeikis and Stewart (1976)]. Deposition velocities obtained in this manner are independent of mass transport and reflect the rates of heterogeneous interactions at the surface that are responsible for removal of the trace species. These, then, represent the maximum deposition velocities that would be encountered in the environment under turbulent atmospheric conditions.

In the studies described here, the reactor was slightly modified so that the inner cylinder consisted of an uncoated portion on the inlet side of the reactor, sufficiently long to permit full development of laminar flow, with the remainder of the cylinder coated with the solid of interest. This permitted use of fully developed laminar flow models for data analysis [Judeikis and Stewart (1976)].

Experiments were carried out at room temperature (20-25 °C) and total pressures of ~500 Torr, except in the case of SO_2. Experiments with the latter species were conducted at ~100 Torr, for the reasons delineated by Judeikis and Stewart (1976). Flow rates were in the range of 1-10 $cm^3\ sec^{-1}$. Reynolds numbers were < 50. Gas mixtures containing traces of H_2S, DMS, or SO_2 generally consisted of ~3-15-percent O_2, with the balance made up of nitrogen and water vapor (0- or 95-percent relative humidity). Trace gas concentrations used were ~15-150 ppm for DMS and SO_2 and ~15-1000 ppm for H_2S. The higher concentrations in the case of H_2S were necessary when

high oxygen concentrations were used because of interference with the H_2S mass spectral peak by the tail of the O_2 peak. All gases were reagent grade quality. Solids used were representative sandy loam and adobe clay soils, taken from the Los Angeles area, and reagent grade Fe_2O_3. Average thicknesses of the solid coatings were ~1 mm, with surface roughnesses of a few tenths of a millimeter.

Diffusion coefficients for SO_2, for use in analysis of the experimental data, were taken from the literature [Fish and Durham (1971)]. Diffusion coefficients for H_2S and DMS were estimated from hard sphere models for binary diffusion [Present (1958)]. In the latter case, we estimate values of 0.268 and 0.180 cm^2/sec, respectively, for H_2S and DMS at 25° C and 500 Torr. Comparison of a large number of values calculated in this fashion for other species, with experimentally measured values for those species, leads us to believe that this method of estimating diffusion coefficients is accurate to better than 10-15 percent. In the experiments described here, the deposition velocities are approximately inversely proportional to the diffusion coefficient. Therefore, uncertainties on the order of 10-15 percent or less in the diffusion coefficients will result in uncertainties of similar magnitude in the deposition velocities.

Background runs were made by passing the appropriate gas mixture through the chamber containing an uncoated cylinder. These runs indicated very small losses of the trace species, probably caused by wall reactions with the Pyrex cylinder. For SO_2 and DMS, and for H_2S removal over Fe_2O_3, these losses were negligible (< 1 percent) compared with those observed when coated cylinders were used. For H_2S removal over soil samples, these losses were on the order of 20-30 percent of those observed when soil samples were present because of the low reactivity of the soils, as discussed in the following section of this appendix. However, since the Pyrex cylinder is coated during an actual experiment, no background corrections were made to the observed data.

Samples for ESCA analysis were prepared by depositing slurries of the appropriate solid in deionized water or reagent grade ethanol onto clean glass slides and evaporating to dryness under vacuum (~10^{-4} Torr). Samples to be exposed to H_2S were then inserted into the cylindrical flow reactor, exposed to H_2S, and subsequently transported in air to the sample chamber of a GCA/McPherson ESCA36 photoelectron spectrometer. Control samples and reference standards were used without H_2S exposure. The ESCA was equipped with a cyropump that allowed spectra to be taken at a pressure of 10^{-9} Torr. The x-ray source for the instrument was a magnesium anode, which emitted electrons at an energy of 1253.6 eV. All peaks were referenced to the carbon 1s peak at 284.6 eV.

RESULTS

Experimental results for H_2S and DMS are given in Table C-1. Included for comparison are deposition velocities for SO_2 measured in this study; the latter values are in good agreement with previous measurements on similar materials [Judeikis and Stewart (1976)]. The deposition velocities reported in Table C-1 were found to be independent of trace gas and oxygen

concentration, as well as relative humidity to within a factor of 2 (except for DMS where relative humidity did have an effect – see below), indicating that surface deposition occurred through first-order or pseudo-first-order processes.

TABLE C-1. MEASURED DEPOSITION VELOCITIES[a]

Solid	Deposition velocity ($cm\ sec^{-1}$)		
	H_2S	DMS	SO_2
Adobe clay soil	0.016	0.28	0.92
Sandy loam soil	0.015	0.064	0.60
Fe_2O_3	0.38		3.9

[a]Values are averages from at least three separate determinations on each of three separate, freshly prepared samples for each material. Uncertainties (resulting from sample-to-sample variations and reproducibilities within samples) are $\sim \pm 20$ percent.

The data given in Table C-1 are for freshly prepared samples. We found that on prolonged exposure to these species, deposition rates gradually decreased and ultimately approached zero. This type of saturation behavior was previously observed for SO_2 [Judeikis and Stewart (1976)] and occurred at $\sim 0.4\text{-}2.8$ g $SO_2\ m^{-2}$ of surface in humidified systems. The behavior is probably the result of depletion of available surface sites for uptake of the trace species because of adsorption of reactant or surface reaction products.

Possible mechanisms for regeneration of active surfaces in the environment, such as interaction with atmospheric ammonia and washing away of soluble surface reaction products by precipitation, were considered in the latter reference and supported by selected experiments carried out in that study. In the case of H_2S, interactions with atmospheric ammonia could also be important. However, surface reaction products of the latter species such as sulfides [see below and Kanivets (1970)] are water insoluble, which precludes washing away by rain water, except as a slurry of particles containing adsorbed surface reaction products.

Ferric oxide was of interest here because of its common occurrence and reported reactivity toward H_2S in soils [Kanivets (1970)]. There was also interest in subjecting Fe_2O_3 samples exposed to H_2S to ESCA analysis. Soil samples could not readily be used for such experiments because of a number of broad background peaks that complicated the signal interpretation.

The results of the ESCA experiments are summarized in Table C-2. Samples of reagent grade $Fe_2(SO_4)_3$, FeS, Na_2SO_3, Fe_2O_3 (blank), and Fe_2O_3 exposed to H_2S were analyzed for the Fe_{3p}, S_{2p}, and C_{1s} peaks.

TABLE C-2. MEASURED BINDING ENERGIES[a]

Sample	Binding energies (eV) Fe_{3p}	S_{2p}
Fe_2O_3 (exposed to H_2S)	55.5	169.0
		160.0
Fe_2O_3 (blank)	56.0	
FeS	55.5	168.4
		161.2[b]
$Fe_2(SO_4)_3$	57-58[c]	169.1
Na_2SO_3		167.6[b]
		166.2
Adobe clay soil	57.1	
Sandy loam soil	56.6	

[a]All binding energies are referenced to C_{1s}.

[b]More intense peak.

[c]Weak, broad peak.

Both the Fe_2O_3 sample exposed to H_2S and the FeS sample have a binding energy (B.E.) of 55.5 eV for the Fe_{3p} peak; this is 0.5 eV less than the B.E. found for the Fe_2O_3 alone. Such a result would not, by itself, indicate that a reaction between the H_2S and Fe_2O_3 had taken place; however, the results of the sulfur analyses are definitive. The unreacted Fe_2O_3 shows no sulfur peak, whereas the Fe_2O_3 sample exposed to H_2S shows two weak peaks at B.E.s of 169.0 and 160 eV. These peak positions are in good agreement with our own measurements for the S_{2p} peaks from $Fe_2(SO_4)_3$ and FeS and with literature values [Craig, Harker, and Novakov (1974)], which indicates that sulfur is present in both the +6 and -2 oxidation states. Such results are consistent with the formation of $FeSO_4$ on the sample surface (for example, from the reduction of Fe^{+3} by H_2S) as well as an indication of the presence of strongly adsorbed sulfide.

It will be noted that the Fe_{3p} peak from $Fe_2(SO_4)_3$ does not agree with that found for Fe_2O_3, although the sulfate S_{2p} peak we have measured agrees with literature values [Craig, Harker, and Novakov (1974)]. Although the Fe_{3p} peak from the ferric sulfate was weak and broad, its position at a B.E. of 57-58 eV was reproducible. At present, we have no explanation for this apparent anomaly.

The weak sulfur peaks observed in the ESCA analyses of Fe_2O_3 exposed to H_2S were in sharp contrast to the strong sulfur (sulfate) peaks observed for various metal oxides exposed to SO_2. These results indicate that much of the H_2S deposited on the Fe_2O_3 surface is weakly adsorbed and is removed during the evacuation of samples to $\sim 10^{-9}$ Torr prior to ESCA analysis. This is not the case for SO_2, where irreversible conversion to adsorbed sulfate appears to be much more extensive.

To test the possibility that deposition of H_2S occurred largely through physical adsorption, we exposed an Fe_2O_3 sample to H_2S until it was nearly saturated, e.g., until the rate of removal of H_2S from the gas stream had decreased by over an order of magnitude. The sample was then evacuated overnight at $\sim 10^{-4}$ Torr and reexposed to H_2S. The result of this experiment indicated that the evacuation restored the reactivity of Fe_2O_3 toward H_2S removal to its initial value, within experimental error ($\sim$20 percent). (This was not the case for SO_2 exposed samples, where reactivity remained low.) From this, we estimate that the deposition velocity for irreversible H_2S removal over Fe_2O_3 is a factor of 5 or more lower than that given in Table C-1.

Similar observations were made for experiments in which the two soils were exposed to DMS until saturated, evacuated overnight ($\sim 10^{-4}$ Torr), and reexposed to DMS. This indicates that here, also, the deposition velocities given in Table C-1 for DMS are largely the result of reversible physical adsorption and that irreversible removal processes occur at much slower rates. Further, we found that DMS deposition from humidified reaction mixtures occurred with velocities < 0.003 cm/sec. The latter results indicate that H_2O competes effectively with DMS for available adsorption sites on the soil surfaces. Additional evidence for this was found when soil samples were exposed to dry DMS reaction mixtures until saturated and subsequently exposed to humidified mixtures. The latter exposure indicated that adsorbed DMS was displaced from the surface by H_2O, as evidenced by an increase of DMS in the gas stream over the input concentration.

DISCUSSION

Results for the two types of soil yield very low deposition rates for H_2S and DMS on these materials and indicate that such materials would be very poor sinks for these reduced sulfur species. [Similarly, Liss and Slater (1974) have estimated a transfer rate of 0.005 cm sec^{-1} for DMS across the air-sea interface, although their estimate is for biogenic emission into the atmosphere.] For example, if an average global atmospheric concentration of 0.2 ppb is assumed for reduced sulfur compounds [Friend (1973) and references therein], deposition velocities of 0.015-0.28 cm sec^{-1} over land areas would result in removal of only $\sim$0.3-5.6 Tg S yr^{-1}, compared with the estimated emission strengths noted above. Although the deposition velocity measured for DMS over adobe clay soil appears to be sufficiently high to be of interest, as noted in the preceding section, this rate appears to be largely the result of reversible adsorption. The deposition velocity for irreversible removal of DMS over this material is considerably lower, perhaps by an order of magnitude or more.

The results obtained for iron oxide are consistent with earlier findings [Kanivets (1970) and references therein] that indicate the latter material is one of the soil components most reactive toward H_2S. Although we did not quantitatively assay our soil samples for Fe_2O_3, ESCA examination of these materials did indicate the presence of small quantities of iron.

Minimal deposition of H_2S or DMS on ground-level surfaces does, of course, indicate the possibility of long-range transport of these species in the atmosphere. In the case of H_2S, however, laboratory measurements indicate a rapid oxidation of this species by OH [Westenberg and de Haas (1973) and Perry, Atkinson, and Pitts (1976)]. Assuming an OH concentration of $\sim 3 \times 10^6$ molecules cm^{-3}, the latter authors estimate a lifetime of ~ 0.5 day for H_2S oxidation in the environment through this reaction.

Similarly, Cox and Sandalls (1974) conclude that the nitric-oxide sensitized photooxidation of DMS would limit the atmospheric lifetime of the latter compound to a few hours; however, as Cadle (1976) points out, the experiments of Cox and Sandalls were conducted with nitrogen oxide concentrations more representative of photochemical smog conditions than those found in the ambient atmosphere.

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